U.S. DEPARTMENT OF COMMERCE
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PB-300 481

Study of the Nature of Ozone, Oxides of Nitrogen, and Nonmethane Hydrocarbons in Tulsa, Oklahoma
Volume I. Project Description and Data Summaries

Research Triangle Inst., Research Triangle Park, NC

Prepared for

Environmental Protection Agency, Research Triangle Park, NC

Apr 79

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-79-008a
April 1979

Air

PB 300481

EPA

Study of the Nature of Ozone, Oxides of Nitrogen, and Nonmethane Hydrocarbons in Tulsa, Oklahoma

Volume I: Project Description and Data Summaries

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/4-79-008a	2.	3. RECIPIENT'S ACCESSION NO. PB300481

4. TITLE AND SUBTITLE Study of the Nature of Ozone, Oxides of Nitrogen, and Nonmethane Hydrocarbons in Tulsa, Oklahoma - Volume I: Project Description and Data Summaries	5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. C. Eaton and F. E. Dimmock	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute Research Triangle Park, NC 27709	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Office of Air Quality Planning and Standards U. S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

EPA

Project Officer: Norman C. Possiel, Jr.

16. ABSTRACT

During the summer of 1977, Research Triangle Institute (RTI) conducted a field measurements program entitled "Study of the Nature of Ozone, Nonmethane Hydrocarbons, and Oxides of Nitrogen in Tulsa, Oklahoma." This volume of the report describes the project and summarizes the data. The monitoring network consisted of eight RTI ground sites and two Tulsa City/County Health Department sites. An airborne measurements program employing a Piper Navaho B was an integral part of the study and is described in detail.

Surface data are summarized through tables of mean daily concentrations, cumulative frequency distributions, and diurnal plots, etc. Also included in this volume are: descriptions and results of the quality control and quality assurance aspects of the field study; an appendix describing the sampling and analytical methodology for GC/FID identification of hydrocarbons; and an appendix describing the sampling and analysis by GC/MS of volatile organic compounds collected on TENAX-GC polymer.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozone Oxides of Nitrogen Non-Methane Hydrocarbons Pollutant Transport		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 219
	20. SECURITY CLASS *(This page)*	22. PRICE PCA10 / MF A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

STUDY OF THE NATURE OF OZONE, OXIDES OF NITROGEN, AND NONMETHANE HYDROCARBONS IN TULSA, OKLAHOMA

VOLUME I

PROJECT DESCRIPTION AND DATA SUMMARIES

by

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Contract No. 68-02-2808

EPA Project Officer: Norman C. Possiel, Jr.

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, N.C. 27711

April 1979

10

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Publication No. EPA-450-4-79-008a

ACKNOWLEDGMENTS

This project was conducted by the Research Triangle Institute (RTI), Research Triangle Park, North Carolina, under Contract No 68-02-2808 for the U.S. Environmental Protection Agency. The support of this agency is gratefully acknowledged as is the advice and guidance of the Project Officer, Norman C. Possiel, Jr., and other staff members of the Office of Air Quality Planning and Standards.

Special acknowledgment is made to personnel of the EPA Environmental Monitoring and Support Laboratory (EMSL) who assisted in the areas of equipment acquisition, data validation, and instrument performance audits. Also acknowledged are staff members of EPA Region VI for supplying mobile laboratories and conducting quality assurance audits.

Mr. L. Byrum, Oklahoma State Department of Health; and Mr. R. Bishop, Mr. R. Randolph, and other staff members of the environmental division of the Tulsa City County Health Department are acknowledged for their unselfish aid in site selection, site preparation, transportation, and data acquisition.

Work on the data presentation portion of this project was performed by staff members of the Systems and Measurements Division of RTI under the general direction of Mr. J. J. B. Worth, Group III Vice President, and Mr. J. B. Tommerdahl, Division Director. Mr. C. E. Decker, Manager, Environmental Measurements Department, was Laboratory Supervisor for this program. Dr. W. C. Eaton served as Project Leader for the ground station program and was responsible for overall coordination and implementation of the program. Mr. J. B. Tommerdahl was Project Leader for the airborne sampling program; Dr. E. D. Pellizzari served as Project Leader for the analysis of organic species collected on Tenax cartridges.

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ABSTRACT

During the summer of 1977, Research Triangle Institute (RTI) conducted a field measurements program entitled "Study of the Nature of Ozone, Nonmethane Hydrocarbons, and Oxides of Nitrogen in Tulsa, Oklahoma." This volume of the report describes the project and summarizes the data.

The monitoring network described in the report consisted of eight RTI ground sites and two Tulsa City/County Health Department sites. These stations were distributed so that one was upwind, four were in, and five were downwind of Tulsa when winds were southerly. Ozone was monitored at 10 sites; NO/NO_x at eight sites; nonmethane hydrocarbons at four sites; wind speed and direction at four sites; and solar radiation at one site. An airborne measurements program employing a Piper Navaho B instrumented for measurement of ozone, NO/NO_x temperature, dew point, b-scat, and condensation nuclei, was an integral part of the study and is described in detail. Morning and afternoon flights were made on 7 selected days that had consistent southerly winds.

Surface data for ozone and oxides of nitrogen are summarized through tables of mean daily concentrations, cumulative frequency distributions, and diurnal plots, etc. Wind speed and direction are summarized by tabulation of frequency of occurrence in 5 mph and 30° increments. Average hydrocarbon concentrations for the several sites are tabulated, and NMHC/NO_x ratios for the 6-9 CDT time period are given. Also included in this volume are: descriptions and results of the quality control and quality assurance aspects of the field study; an appendix describing the sampling and analytical methodology for GC/FID identification of hydrocarbons; and an appendix describing the sampling and analysis by GC/MS of volatile organic compounds collected on TENAX-GC polymer.

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SECTION 1.0

INTRODUCTION

1.1 BACKGROUND

The phenomenon of photochemical smog occurs in most urban areas of the world. These urban centers represent geographically concentrated sources of primary pollutants such as nitrogen oxides (NO_x) and hydrocarbons (HC). Hydrocarbons and oxides of nitrogen in the presence of sunlight undergo a complex sequence of photochemical reactions resulting in the accumulation of ozone (O_3). The relationship between initial concentrations of ozone precursors (HC and NO_x) and the resulting maximum ozone levels is highly nonlinear. This has been illustrated frequently by smog chamber results and by predictions of computer-based photochemical models. The relationship may be represented in two dimensions by equal concentration lines (isopleths) of ozone maxima as a function of initial HC and NO_x concentrations.

The National Ambient Air Quality Standard (NAAQS) for photochemical oxidants at the time of this study was: a maximum 1-hr concentration of 0.08 ppm is not to be exceeded more frequently than once per year. In 1979 the NAAQS standard was revised to 0.12 ppm. Strategies directed at achieving this goal are aimed at controlling oxidants by reducing emissions of the hydrocarbon precursors. Current control strategies are based on Appendix J, Part 51, Title 40 of the Code of Federal Regulations. Questions have been raised concerning the applicability of the Appendix J approach, and alternatives based on the oxidant-precursor relationship are being explored.

An alternate known as the isopleth approach is currently under consideration. This approach is based on the previously described relationship between initial HC and NO_x and the corresponding daily maximum O_3 levels represented as isopleths. It is described fully in a current EPA document, "Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships between Photochemical Oxidants and Precursors."[1] The technique requires a significant accumulation of ambient air data (HC, NO_x, O_3) and has not been extensively validated. The isopleth approach may not be directly applicable to controlling excessive ozone levels resulting from multi-day, long-range transport, although transported ozone is considered in the approach. This study addresses single-day, nontransport urban conditions and short-range transport situations in which the oxidant precursor relationships are similar. The purpose of this field study was to collect data that can be used to test the isopleth approach and other models.

1.2 RESEARCH OBJECTIVES

The principal objective of the field measurement program was to provide a high quality pollutant and meteorological data base to EPA for use in operating various photochemical simulation models. The data base will also be analyzed to: (1) understand the spatial distribution of ozone, oxides of nitrogen, and nonmethane hydrocarbon species concentrations (including hydrocarbons in the vicinity of a medium-sized city); (2) examine the relationship between ambient nonmethane hydrocarbon/NO_x ratios and maximum measured ozone concentrations observed downwind; (3) determine or obtain a measure of the upwind ozone concentrations coming into the city; and (4) document ozone transport across the study region.

SECTION 2.0

OVERVIEW OF THE STUDY

2.1 GENERAL DESCRIPTION OF GROUND STATION MONITORING NETWORK

The monitoring program designed to meet the specifications and requirements of this study consisted of air quality and meteorological measurements at eight ground stations located upwind of, in, and downwind of Tulsa, Oklahoma, during the period from July 1 through September 30, 1977. The following measurements were made at the selected sites: ozone was measured at one site 36 km upwind, two sites downtown, and five sites downwind to 25-50 km; oxides of nitrogen were measured at each of the sites mentioned above; total and nonmethane hydrocarbons were sampled at the two downtown sites; nonmethane hydrocarbon integrated samples were collected from 0600 to 0900 CDT for individual species analysis at the upwind site and the two downtown sites. Wind speed and wind direction were recorded upwind, downtown, and at four sites downwind to characterize the airflow across the area. Solar radiation was recorded at the two sites 25-30 km downwind. Further details concerning site locations, instrumentation, calibration techniques, and quality control procedures used in conducting the field measurement program are described in the following subsections.

2.1.1 Monitoring Network

A brief examination of the historical meteorological records for the Tulsa, Oklahoma, area indicated that prevailing winds during June, July, August, and September are from the southerly direction approximately 60 percent of the time with an average wind speed of 4 m/s (9 mph). Based on this information and the objectives of the measurement program, the station deployment shown in Figure 2.1 was established for the air monitoring network. Each circle represents a sampling station; the symbols included inside each circle indicate the air quality and meteorological parameters that were measured at each site. The two downtown monitoring stations were employed to establish the NMHC/NO_x ratios in downtown Tulsa; the five generally downwind stations were placed on arcs at distances of 15, 25, and 50 km to provide broad downwind coverage of ozone and oxides of nitrogen concentrations; the one upwind station obtained a measure of the upwind ozone concentrations coming into the city.

2.1.2 Instrumentation for Continuous Monitoring

Continuous measurement methods were used to acquire data for ozone, oxides of nitrogen, nonmethane hydrocarbons, wind speed, wind direction, and solar radiation at the stations shown in Figure 2.1. Brief descriptions of the measurement principles for each parameter are presented in the following paragraphs.

2.1.2.1 Ozone--

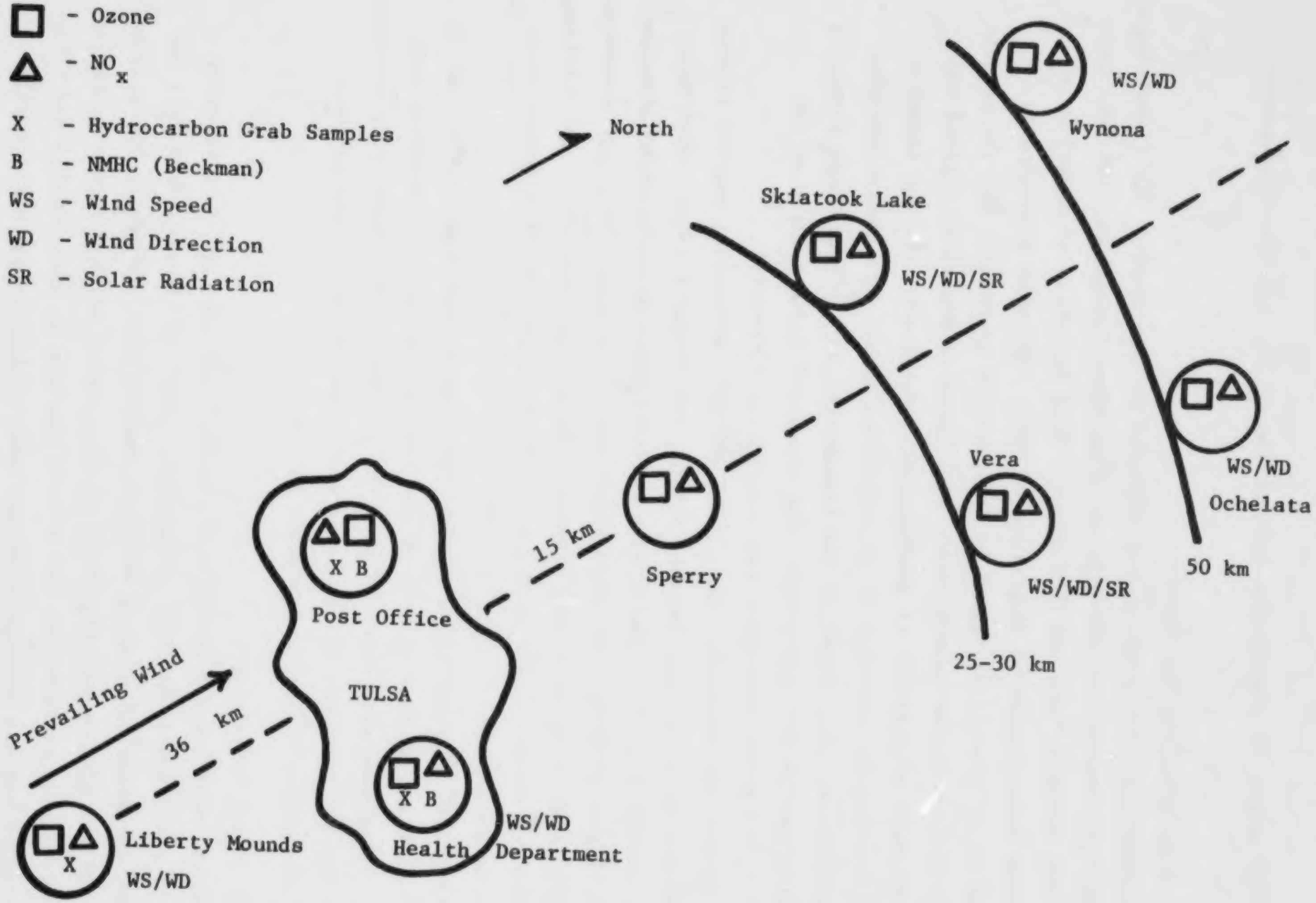
Ambient ozone concentrations were measured at all sites using the Bendix Model 8002 chemiluminescent ozone analyzer. The principle of operation of this instrument is based on the gas-phase chemiluminescent reaction between ethylene and ozone. The reliability, stability, specificity, and precision of ozone measurements by this technique have been adequately demonstrated and described in the literature.[2]

2.1.2.2 Oxides of Nitrogen--

Nitric oxide and nitrogen dioxide concentrations were measured at all eight ground stations using the Bendix Model 8101-B NO-NO_2-NO_x analyzer. The principle of operation of this instrument is based on the gas-phase chemiluminescent reaction between NO and O_3. Measurement of the NO_2 concentration by this method requires that NO_2 be reduced to NO, which then reacts with O_3. The sum of the initial NO measurement plus the NO produced by the reduction of NO_2 is the nitrogen oxides (NO_x) measurement. Electronic subtraction of the NO measurement from the NO_x measurement gives the NO_2 concentration.

2.1.2.3 Nonmethane Hydrocarbons--

Nonmethane hydrocarbon (NMHC) concentrations were measured at two ground stations using the Beckman Model 6800 air quality chromatograph, which utilizes an automatic gas chromatographic-flame ionization detector (GC-FID) to measure THC and CH_4 in ambient air. The NMHC concentration of



□ - Ozone
△ - NO_x
X - Hydrocarbon Grab Samples
B - NMHC (Beckman)
WS - Wind Speed
WD - Wind Direction
SR - Solar Radiation
North
Wynona
WS/WD
Skiatook Lake
WS/WD/SR
Ochelata
WS/WD
50 km
Vera
WS/WD/SR
25-30 km
Sperry
15 km
Post Office
X B
TULSA
Health Department
X B
WS/WD
Prevailing Wind
36 km
Liberty Mounds
X
WS/WD

Figure 2.1. Air monitoring network for Tulsa, Oklahoma study

the ambient sample is computed by subtraction of CH_4 from the THC measurement.

2.1.2.4 Wind Direction and Speed--

Two different wind sensors were employed in this study. The Climatronics Wind Direction Transmitter (WD-10B) and Wind Speed Transmitter (WS-10A) were used at the Skiatook Lake and Vera sites. Wind direction is sensed by a lightweight counterbalanced vinyl-covered vane. The wind direction is converted to an electrical signal by a capacitive transducer and the associated electronics of the transmitter. Wind speed is sensed by a three-cup anemometer made of plastic. A photochopper rotates with the cup assembly and its rotation is converted to an electrical signal by a phototransistor and light source. The output of the transmitter is a signal whose frequency is proportional to the wind speed. The threshold for operation of the sensors is 0.2 m/sec (0.5 mph); the accuracy is ±1 percent.

A Meteorology Research, Inc., Model MRI-1072 mechanical weather station was employed at the Liberty Mounds, Wynona, and Ochelata sites. With this system, wind direction is sensed by a ball-bearing-mounted balanced aluminum blade with nose damping. The wind speed (run) is measured by a cup anemometer employing three 12 cm (4.5 in.) diameter conical aluminum cups. The starting threshold for either sensor is 0.3 m/sec (0.75 mph); overall accuracy is ±2 percent of full scale.

Difficulties in operation of the Climatronics wind sensors resulted in the invalidation or loss of most of the data at the Vera and Skiatook Lake sites. Other wind data were obtained for the Health Department site (courtesy of the Tulsa City/County Health Department) and the Tulsa International Airport (courtesy of National Weather Service).

2.1.2.5 Solar Radiation--

Solar radiation was measured at the Skiatook Lake and Vera sites by means of a silicon solar cell pyranometer. Much of the data from Vera was lost due to sensor downtime or moisture condensation problems. The millivolt output of the pyranometer is converted to a linear voltage versus radiation by the radiation translator. The sensor responds to both visible and ultraviolet light and was calibrated by the manufacturer versus a thermopile sensor, which responds to all solar radiation. Data are reported in units of Langleys min^{-1}, hourly average.

Table 2.1. Calibration techniques

Pollutant	Calibration technique
Ozone	Ultraviolet ozone generator referenced to NBS-SRM (NO in nitrogen) by Gas Phase Titration (GPT).
Nitric oxide, nitrogen dioxide	Gas Phase Titration technique using NBS-SRM (NO in nitrogen) standard.
Total hydrocarbon, methane	Compressed gas cylinders containing methane, referenced to QAB-EMSL standards for methane.

2.1.3 Calibration Techniques

Dynamic techniques which were used to calibrate each ambient air analyzer at monthly intervals during the 90-day period of field operations are outlined in Table 2.1. Similar procedures and standards were used for performing daily zero and span checks. A brief description of the calibration techniques is given below.

2.1.3.1 Ozone-Ultraviolet Ozone Generator Referenced to NBS-SRM NO in Nitrogen Standard--

Dynamic calibration of the ozone analyzers was accomplished by use of an ultraviolet ozone generator. The ozone generator consists of a mercury vapor lamp 20 cm (8 in.) in length that irradiates a 16-mm (5/8-in.) diameter quartz tube through which clean (compressed) air flows at 5 L/min. Ozone concentrations over the measurement range are generated by variable shielding of the mercury vapor lamp. Although the ultraviolet ozone generator has been shown to be quite stable and reproducible, the gas phase titration procedure was used as the reference method.[3]

2.1.3.2 Nitric Oxide/Nitrogen Dioxide: Gas Phase Titration Technique--

The gas phase titration technique was used for dynamic calibration of the chemiluminescent NO-NO_2-NO_x analyzers.[3] The technique is based on the rapid gas-phase reaction between nitric oxide and ozone to produce a stoichiometric quantity of nitrogen dioxide. A certified tank of nitrogen (of an approximate concentration of 50 ppm by volume) is diluted with zero air to provide NO concentrations in the range of 0.015 to 0.8 ppm. Nitrogen dioxide concentrations are produced by the reaction of NO with ozone. Primary calibration of the NO in nitrogen concentration was accomplished by reference to an NBS-SRM. The NO concentration of each cylinder used was referenced to the NBS-SRM prior to going to the field and at the conclusion of the study.

2.1.3.3 Total Hydrocarbons/Methane/Nonmethane Hydrocarbons--

Calibration of the Beckman 6800 air quality chromatograph was accomplished using cylinders containing known concentrations of methane in air according to procedures in the Federal Register.[4] Mixtures of methane in air were purchased from Airco, Inc., and referenced to appropriate methane standards maintained at QAB-EMSL.

2.1.4 Quality Control Program

To achieve and maintain a high level of confidence in air quality data, it is essential to routinely monitor critical instrument parameters and to maintain appropriate records. In general, quality control for the Tulsa oxidant study included verification and referencing of calibration standards to NBS-SRM's; daily, weekly and monthly operational and maintenance checks; daily zero and span checks; monthly dynamic calibrations; maintenance of analyzer logs, use of control charts, use of standard stripchart data reduction procedures; and thorough training of instrument operators.

Calibration data, as well as daily zero and span information, were examined for excessive zero and span drift. When zero drift exceeded ±2 percent of full scale per 24-hr period, the data of the preceding 24-hr period were considered to be of questionable validity and were critically examined and invalidated if necessary. Span drift was determined on a daily basis and from multipoint calibration data every month. If the span drift exceeded ±15 percent per 24-hr period, the data were invalidated and an immediate recalibration of the instrument was performed.

The pollutant and meteorological data were reduced from the strip chart records daily and entered as hourly averages on Storage and Retrieval of Aerometric Data (SAROAD) forms. The reduced data were visually compared to the strip charts and examined for completeness, accuracy, signs of equipment malfunctions, excessive pollutant levels, and any unusual diurnal patterns.

EPA maintained a routine performance audit program for the Tulsa study. The audit data provided external quality assurance and served as a measure of the quality of data generated during the study. A more detailed discussion of the quality control program is provided in Section 5.0.

2.2 SAMPLING AND ANALYSIS FOR HYDROCARBONS IN AMBIENT AIR

While many different types of sampling containers have been employed in collecting hydrocarbons, few have been found to be adequate for the collection of C_2-C_{10} hydrocarbons. The most widely used sampling containers are polymeric film sampling bags (Tedlar, Teflon), glass bulbs, stainless steel containers, and solid absorbents. Each container has advantages and disadvantages.[5] [6]

2.2.1 Sample Collection: Stainless Steel Containers

Stainless steel containers are very durable and easily deployed in field programs. The storage capability of trace organics in passivated stainless steel containers is excellent.[7] For these reasons, stainless steel containers were chosen for use in this study. These containers were cleaned in the laboratory by a series of heated, high vacuum evacuations.

Two metal bellows pumps were employed to fill the stainless steel container. One, a Model MB-41, sampled directly from the station's ambient air manifold at a rate of several liters per minute to insure that a representative sample was obtained. A second pump, Model MB-151, sampled from a tee on the outlet side of the MB-41 pump. The larger MB-151 pump provided adequate pressure to insure a constant flow rate through a critical orifice into the container. A flow rate of 15 cc/min was sufficient to fill the sampling container to a pressure of 3-5 psig in 3 hr. At the completion of the sampling period, the sampling container was sealed and shipped back to RTI for analysis. In order to minimize the time between sampling and analysis, sample containers were shipped by air freight.

Details of quality control and quality assurance procedures associated with the hydrocarbon sampling program are given in Section 5.0. Sampling and analytical methodology are discussed in Appendix A of this volume.

2.3 AIRBORNE MONITORING PROGRAM

An airborne measurements program consisting of horizontal traverses and vertical spirals was included in the study design. Ten days of flights were conducted to obtain data on the morning atmosphere above and below the mixing layer; the afternoon atmosphere within the mixing layer; the level of pollutants upwind, over, and downwind of Tulsa; and any single source or complex sources that might affect the atmosphere within the Tulsa area.

Both transport and stagnation pattern flights were planned. A thorough discussion of the airborne measurements program is given in Section 4.0.

2.4 ORGANIC SPECIES IDENTIFICATION BY TENAX-GC/MS/COMP

Another element of the study design was collection of ambient air samples on Tenax GC for GC/MS/COMP analysis of organic species. The mass spectra were interpreted to ascertain the qualitative composition of the organic components in Tulsa's downtown air and air at other sites. The GC/MS data analyses provide positive identification of the organic constituents collected and provide confirmation of the qualitative identification of hydrocarbons that were collected in stainless steel containers and analyzed by GC/FID.

Complete details on the GC/MS/COMP analysis method are given in Appendix B of this volume.

SECTION 3.0

FIELD MEASUREMENT PROGRAM

This section provides a description of the protocol followed in establishing and operating the ground station sampling network for the Tulsa summer study. Site locations, instrumentation, data acquisition, and data processing and presentation procedures are discussed below.

3.1 GROUND STATIONS

3.1.1 Siting Considerations

Tulsa, Oklahoma, is a medium-sized city (population 350,000) situated in a region characterized by gently rolling pastureland. Due to the city's geographic isolation from other urban areas, Tulsa is an ideal location for a study of pollutant chemistry and transport. Analysis of the Tulsa study data base is expected to provide a better understanding of the spatial distribution of ozone, oxides of nitrogen, and hydrocarbon species in and near a mid-sized city.

Historical meteorological records for the Tulsa, Oklahoma, area indicate prevailing winds during July through September are southerly at an average speed of 4 m/s (9 mph). Since two of the objectives of the program were to determine the concentrations of ozone, oxides of nitrogen, and hydrocarbons transported into the city and the impact of local emissions on downwind ozone and precursor concentrations, an eight-station network was established along the prevailing wind direction.

One station, Liberty Mounds, was located approximately 37 km (23 mi) south of downtown Tulsa. This station provided information on the background concentrations of air masses entering the city during periods of southerly winds. Two monitoring stations were located within the Tulsa city limits. The Post Office site, located in the central business district, was within 3.2 km (2 mi) of an oil refinery complex and a major interstate highway traffic interchange. The other site, Tulsa City/County Health Department, was in a residential/commercial area of the city.

Five stations were located to the north of Tulsa. The closest site was at Sperry, Oklahoma, approximately 15 km (10 mi) from the Tulsa Post Office site. Two other sites, Skiatook Lake and Vera, were each approximately 30 km (20 mi) from the central Tulsa area. The northern-most sites were at Wynona and Ochelata, each about 50 km (30 mi) from the Tulsa Post Office site.

The location of each of the monitoring sites is shown in the map in Figure 3.1. The linear distance between the various sites is presented in Table 3.1, and the SAROAD number and geographic coordinates for each site are listed in Table 3.2.

Two other ozone monitoring stations were operated by the Tulsa City/County Health Department. These sites were located within the city limits at the corner of Mohawk and Peoria Streets and at the corner of Apache and Sheridan Streets. The reader should note that the ozone monitors at these two sites were calibrated by the use of the neutral buffered potassium iodide (NBKI) procedure, not the gas phase titration (GPT) procedure that was used at the eight stations in the present study. A laboratory comparison of these two calibration procedures, conducted at EPA's EMSL-QAB laboratory during the period of the study, has shown that the ozone concentrations determined by the analyzers referenced to NBKI are approximately 20 percent higher than those referenced by gas phase titration.

3.1.2 Descriptions of Monitoring Stations

3.1.2.1 Liberty Mounds--

This site was located in a rural area of Okmulgee County, on property owned by the rural water works, District No. 6. The area immediately adjacent to the site is illustrated in Figure 3.2. All ambient air analyzers and associated equipment were housed in a 2.4-m by 4.8-m air conditioned Avion trailer. Wind direction (WD) and speed (WS) were measured with an MRI mechanical weather station, which was mounted on a 4-m (13-ft) tripod. The tripod was located approximately 9 m (30 ft) west of the trailer. The station was located approximately 45 m to the north of a hard-surfaced road and 2 km east of the U.S. Highway 75. The sampling inlet was located on the south end of the trailer at a height of 4 m above the ground. Surface elevation was 216 m. Exposure was excellent in all directions.

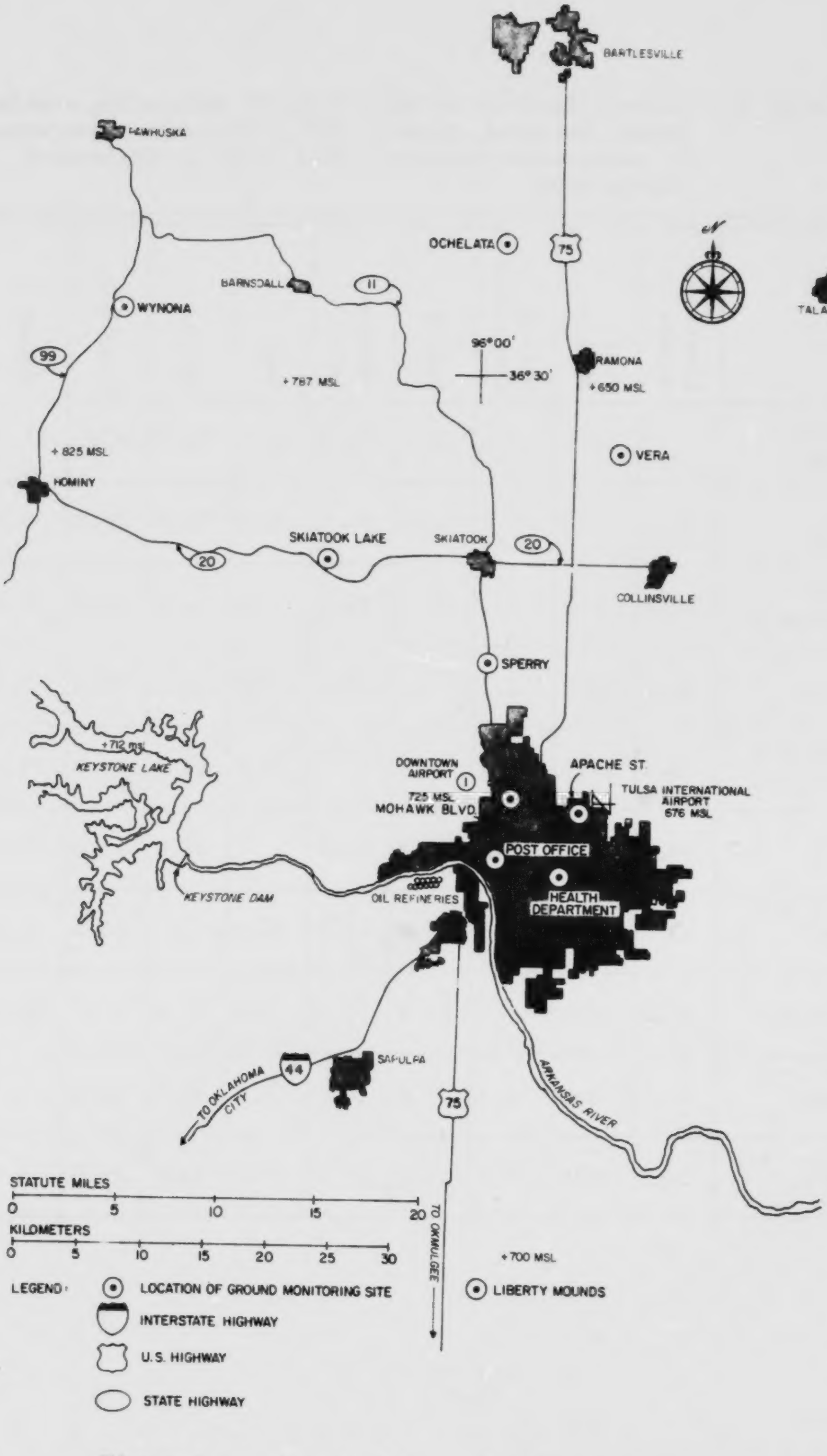

BARTLESVILLE
NOWATA
PAWHUSKA
N
OCHELATA
75
BARNSDALL
11
WYNONA
TALALA
99
96°00'
36°30'
RAMONA
+787 MSL
+650 MSL
+825 MSL
VERA
HOMINY
SKIATOOK LAKE
SKIATOOK
20
20
COLLINSVILLE
SPERRY
+712 msl
KEYSTONE LAKE
DOWNTOWN AIRPORT
725 MSL
MOHAWK BLVD.
APACHE ST.
TULSA INTERNATIONAL AIRPORT
676 MSL
POST OFFICE
HEALTH DEPARTMENT
KEYSTONE DAM
OIL REFINERIES
SAPULPA
44
TO OKLAHOMA CITY
75
ARKANSAS RIVER
STATUTE MILES
0
5
10
15
20
KILOMETERS
0
5
10
15
20
25
30
TO OKMULGEE
+700 MSL
LIBERTY MOUNDS
LEGEND:
LOCATION OF GROUND MONITORING SITE
INTERSTATE HIGHWAY
U.S. HIGHWAY
STATE HIGHWAY

Figure 3.1. Map of Tulsa, Oklahoma and vicinity.

Table 3.1. Linear distances in miles between monitoring stations, Tulsa, Oklahoma, summer, 1977. Distances determined by measurement between points on U. S. Geological Survey maps

	Liberty Mounds	Post Office	Health Department	Sperry	Skiatook Lake	Vera	Wynona	Ochelata	Mohawk	Apache
Liberty Mounds		22.5	20.5	32.5	38.5	45.0	53.0	52.0	24.7	24.0
Post Office	22.5		4.5	10.0	16.0	21.5	34.0	30.0	3.0	5.4
Health Department	20.5	4.5		11.7	19.0	23.0	36.0	31.0	4.8	3.7
Sperry	32.5	10.0	11.7		8.8	12.3	26.0	21.0	7.0	8.8
Skiatook Lake	38.5	16.0	19.0	8.8		15.4	14.0	20.0	14.0	17.0
Vera	45.0	21.5	23.0	12.3	15.4		26.0	12.0	18.5	19.0
Wynona	53.0	34.0	36.0	26.0	14.0	26.0		20.0	32.0	35.0
Ochelata	52.0	30.0	31.0	21.0	20.0	12.0	20.0		28.5	29.0
Mohawk	24.7	3.0	4.8	7.0	14.0	18.5	32.0	28.5		4.0
Apache	24.0	5.4	3.7	8.8	17.0	19.0	35.0	29.0	4.0	

Table 3.2. Tulsa, Oklahoma monitoring sites; SAROAD identification.

Station Name	SAROAD Number	Coordinates
Liberty Mounds	372240999	Longitude W 95 59 56 Latitude N 35 50 34
Post Office	373000998	Longitude W 95 59 49 Latitude N 36 09 11
City/County Public Health Department	373000997	Longitude W 95 55 26 Latitude N 36 08 26
Sperry	373020996	Longitude W 95 59 23 Latitude N 36 17 51
Skiatook Lake	372260995	Longitude W 96 07 35 Latitude N 36 21 23
Vera	373140994	Longitude W 95 52 58 Latitude N 36 26 56
Wynona	372260993	Longitude W 96 19 21 Latitude N 36 32 37
Ochelata	373140992	Longitude W 95 58 57 Latitude N 36 35 40
Mohawk Boulevard	373000127	Longitude W 95 58 28 Latitude N 36 07 49
E. Apache Street	373000132	Longitude W 95 54 19 Latitude N 36 11 31

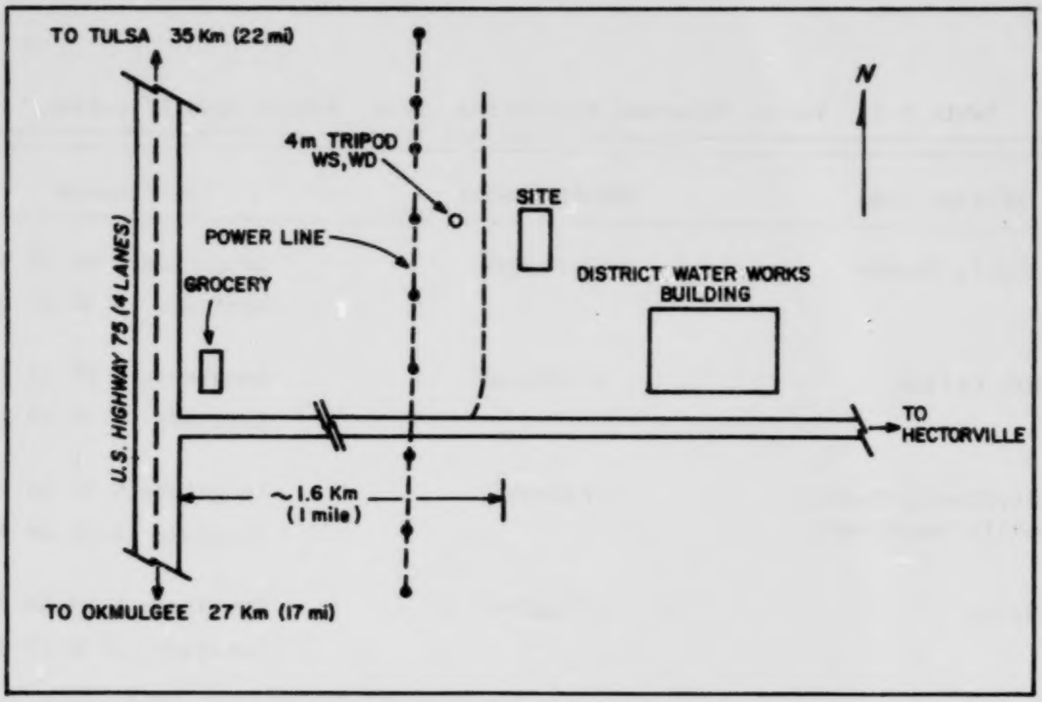

TO TULSA 35 Km (22 mi)
N
4m TRIPOD WS, WD
SITE
POWER LINE
GROCERY
DISTRICT WATER WORKS BUILDING
U.S. HIGHWAY 75 (4 LANES)
TO HECTORVILLE
~1.6 Km (1 mile)
TO OKMULGEE 27 Km (17 mi)

Figure 3.2. Air monitoring site, near Liberty Mounds, Oklahoma.

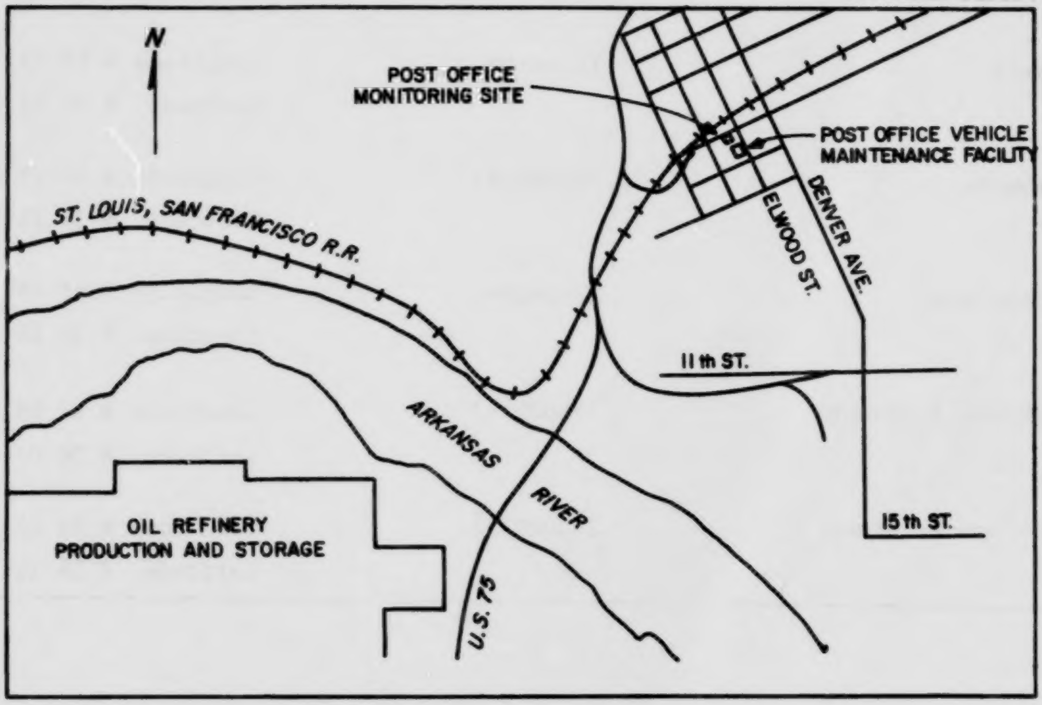

N
POST OFFICE MONITORING SITE
POST OFFICE VEHICLE MAINTENANCE FACILITY
ST. LOUIS, SAN FRANCISCO R.R.
ELWOOD ST.
DENVER AVE.
11th ST.
ARKANSAS RIVER
15th ST.
OIL REFINERY PRODUCTION AND STORAGE
U.S. 75

Figure 3.3. Air monitoring site, U. S. Post Office Vehicle Maintenance Facility, Tulsa.

3.1.2.2 Tulsa Post Office--

This monitoring station was located in the northwest corner of property occupied by the U.S. Postal Service. The facility is located at the southwest corner of Second and Elwood Streets (see Figure 3.3). Ozone, NO_x, and hydrocarbon analyzers, and associated equipment were housed in a 3-m by 5.5-m air conditioned Coastal trailer. The station was 1.1 km (0.7 mi) northeast of a major traffic interchange, 1.6 km (1 mi) northeast of the Arkansas River, and 2.3 km (1.4 mi) northeast of the two petroleum refineries. The sampling inlet was positioned on the west side of the trailer at a height of 4.6 m above the pavement. The site elevation was 209 m above mean sea level. Exposure at this site was relatively good from the south, west, and north; however, exposure from the east was somewhat obstructed by buildings in the adjacent block.

3.1.2.3 Tulsa City/County Health Department--

This station was located in the northeast corner of the Tulsa State Fairgrounds, approximately 100 m from the corner of 15th Street and Yale Avenue (see Figure 3.4) The ozone, oxides of nitrogen, and nonmethane hydrocarbon analyzers and associated equipment were maintained in a 4.8-m by 13.7-m air conditioned trailer. The trailer was approximately 76 m southeast of the Tulsa City/County Health Department building. The air sample inlet was located at the southeastern end of the trailer at a height of 4.9 m above the surface. The area surrounding the fairgrounds was primarily residential and commercial. Exposure was good in all directions except for the northwest. Wind speed and direction sensors were maintained at this site by Health Department personnel. The sensors were mounted on a 10 m tower atop the three-story Health Department building.

3.1.2.4 Sperry--

This site was located adjacent to the National Guard Armory at Sperry, Oklahoma (population 1,300), which is 16 km (10 mi) north of the Tulsa Post Office site. The station was anchored in the southwest corner of the Armory lot as shown in Figure 3.5. The elevation of the station was 190 m above mean sea level. The ozone and oxides of nitrogen analyzers were housed in an environmentally controlled room at the south end of a 4.3-m by 10.7-m trailer. The sampling inlet was 4.8 m above the ground. Exposure at this station was good in all directions.

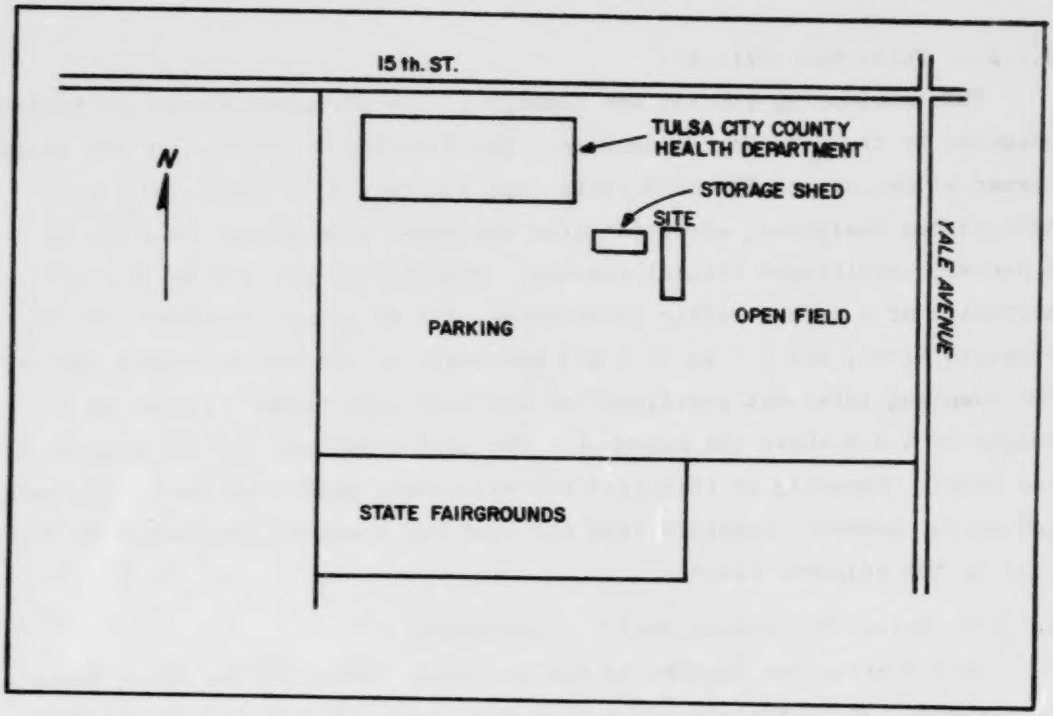

15 th. ST.
TULSA CITY COUNTY HEALTH DEPARTMENT
N
STORAGE SHED
SITE
YALE AVENUE
PARKING
OPEN FIELD
STATE FAIRGROUNDS

Figure 3.4. Air monitoring site, Tulsa City/County Health Department.

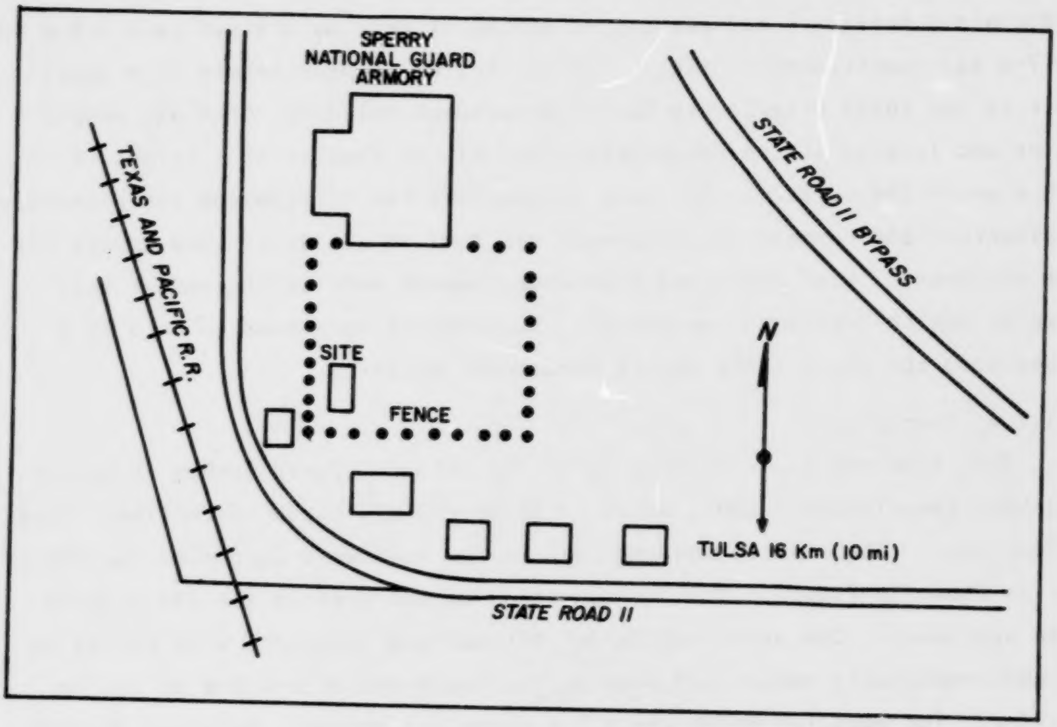

SPERRY NATIONAL GUARD ARMORY
STATE ROAD 11 BYPASS
TEXAS AND PACIFIC R.R.
N
SITE
FENCE
TULSA 16 Km (10 mi)
STATE ROAD 11

Figure 3.5. Air monitoring site, Sperry, Oklahoma.

3.1.2.5 Skiatook Lake--

This site, illustrated in Figure 3.6, was located in a rural, hilly area about 26 km northwest of Tulsa and about 11.5 km west of Skiatook, Oklahoma. At this station, the ozone and oxides of nitrogen analyzers and associated equipment were maintained in an air conditioned 3-m by 4.3-m Teton trailer. Exposure at this rural site was excellent. The site elevation was 201 m above mean sea level and the sample inlet, located at the northwestern corner of the trailer, was positioned 4 m above the surface. The meteorological system (Climatronics Corporation), consisting of an anemometer, wind vane, and a solar radiometer, was sited on a 10-m (32-ft) tower approximately 27 m (90 ft) north of the trailer.

3.1.2.6 Wynona--

The northwestern-most monitoring station was located on the grounds of the Wynona Trailer Court in Wynona, Oklahoma (pop. 1,000), approximately 54.7 km (34 mi) northwest of Tulsa. The area surrounding the site is rural and the terrain is fairly flat. Exposure at this station was excellent in all directions. The ozone, oxides of nitrogen, and hydrocarbon analyzers were maintained in an air conditioned 2.4-m by 4.3-m Atlantic trailer as shown in Figure 3.7. The sample inlet was placed on the south side of the trailer 5.2 m above the ground. The site altitude was 271 m above the mean sea level. A 4.5-m tripod supported an MRI WS/WD measurement system and was located approximately 6 m to the east of the trailer.

3.1.2.7 Vera--

This monitoring station was located in Vera, Oklahoma (population 350), 34.6 km northeast of Tulsa. The ozone and oxides of nitrogen analyzers were sited in a 2.4-m by 4.9-m air conditioned Avion trailer located 36.5 m southwest of the Vera Post Office building. Figure 3.8 illustrates the area. The sample inlet was located on the southwestern corner of the trailer at a height of 4.3 m above the surface. Altitude of the site was approximately 199 m above mean sea level. A 10-m tower located 9.1 m east of the trailer supported Climatronics WS/WD and solar radiation sensors. Exposure at this site may have been somewhat limited from the southeast due to an oak tree, 15 m tall, located 45 m from the meteorological tower.

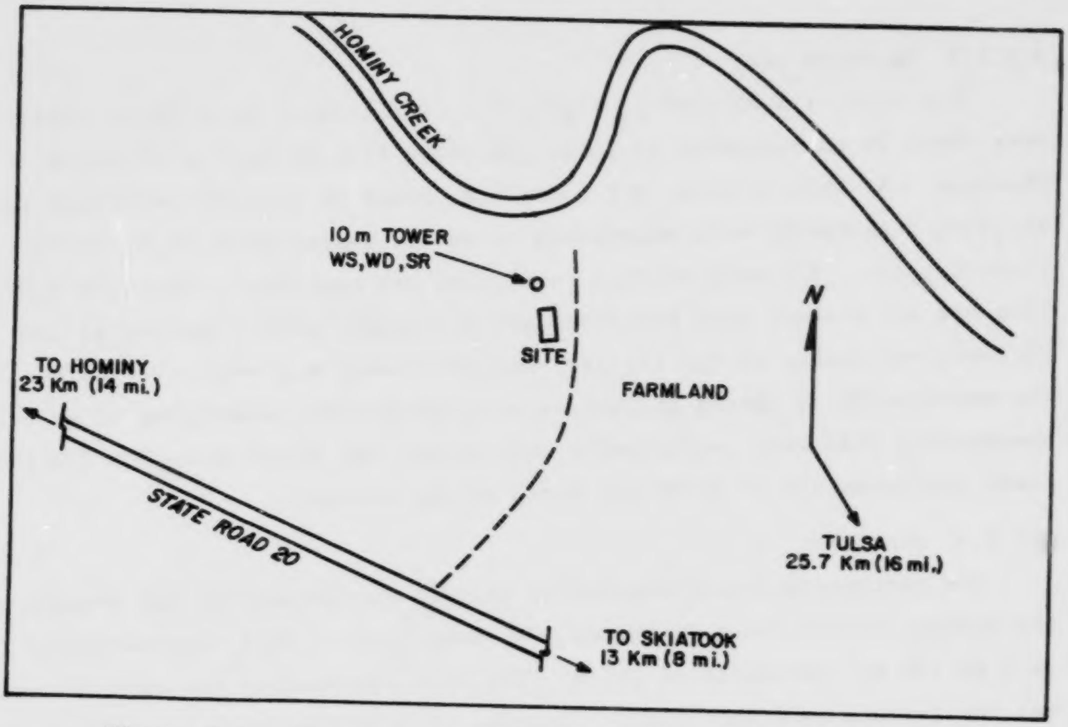

HOMINY CREEK
10 m TOWER
WS,WD,SR
SITE
TO HOMINY
23 Km (14 mi.)
FARMLAND
N
STATE ROAD 20
TULSA
25.7 Km (16 mi.)
TO SKIATOOK
13 Km (8 mi.)

Figure 3.6. Air monitoring site, near Skiatook, Oklahoma.

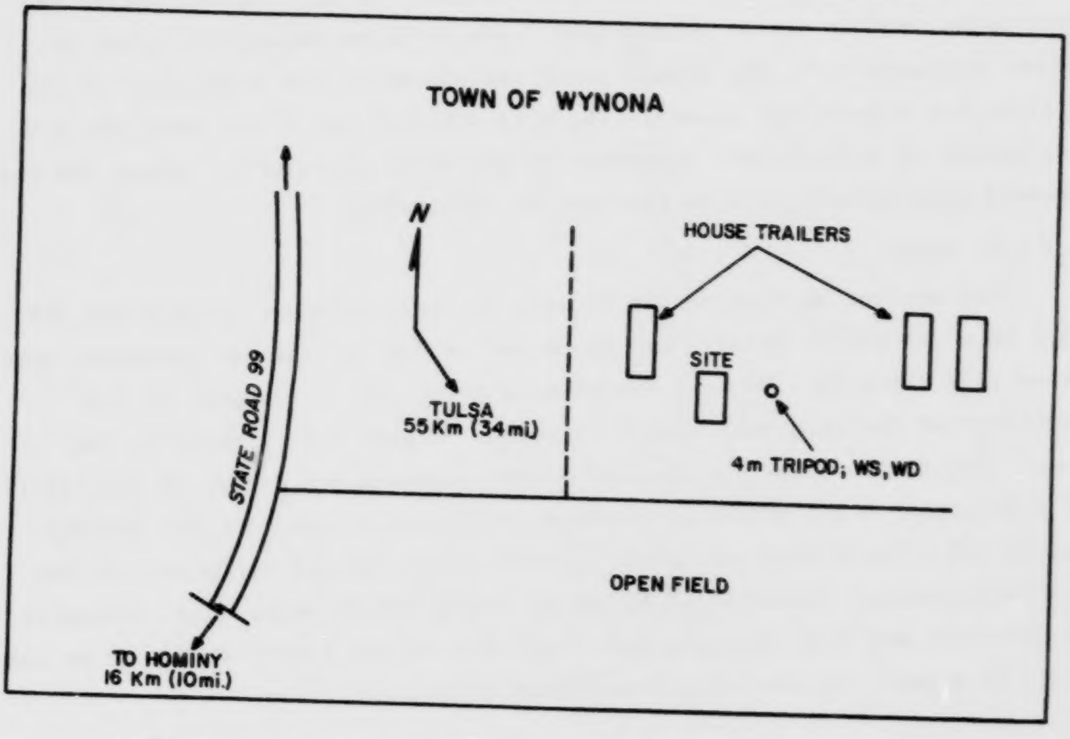

TOWN OF WYNONA
N
HOUSE TRAILERS
STATE ROAD 99
SITE
TULSA
55 Km (34 mi)
4 m TRIPOD; WS, WD
OPEN FIELD
TO HOMINY
16 Km (10mi.)

Figure 3.7. Air monitoring site, Wynona, Oklahoma.

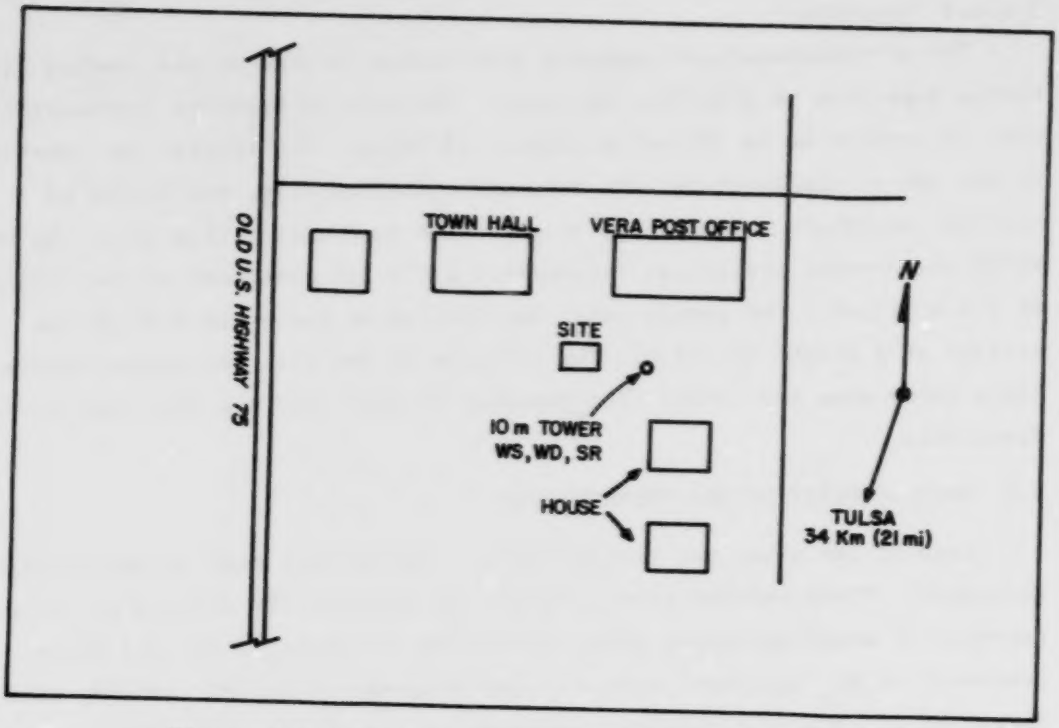

OLD U.S. HIGHWAY 75
TOWN HALL
VERA POST OFFICE
SITE
10 m TOWER
WS, WD, SR
HOUSE
N
TULSA
34 Km (21 mi)

Figure 3.8. Air monitoring site, Vera, Oklahoma.

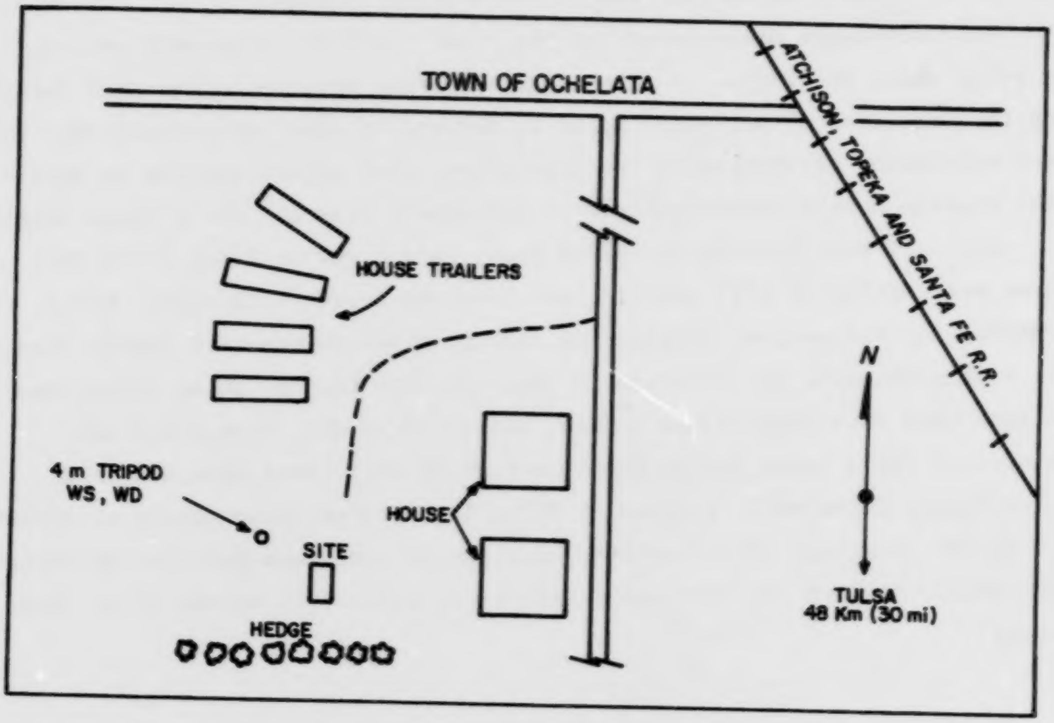

TOWN OF OCHELATA
ATCHISON, TOPEKA AND SANTA FE R.R.
HOUSE TRAILERS
N
4 m TRIPOD
WS, WD
SITE
HOUSE
HEDGE
TULSA
48 Km (30 mi)

Figure 3.9. Air monitoring site, Ochelata, Oklahoma.

3.1.2.8 Ochelata--

The northeastern-most sampling station was located at the Country Aire Mobile Home Park in Ochelata, Oklahoma. The town of Ochelata (population 500) is located 48 km (30 mi) northeast of Tulsa. The trailer was identical to the one at the Skiatook Lake site and contained ozone and oxides of nitrogen analyzers. Figure 3.9 diagrams the features of this site. An MRI WS/WD measurement system was located 9.1 m (30 ft) southwest of the trailer on a 4-m tripod. The sample inlet was located on the south side of the trailer at a height of 3.7 m. The altitude of the site was approximately 230 m above mean sea level. The exposure at this site was excellent in all directions.

3.2 DATA ACQUISITION AND PRESENTATION

Each of the sites was visited daily. Checks were made of analyzers and recorders. Items checked were: supply gas pressure and flow rates; vacuum pressure of sampling pumps; proper operation of valves, fans, and ozone generator of NO_x analyzer; zero and span response of O_3, NO, and NO_2 channels; operation of catalytic ethylene oxidizer. All readings and comments were entered on a daily checksheet and in the station logbook.

All continuous measurements at the eight field stations were recorded on strip chart recorders. A least squares linear regression equation relating concentration of pollutant (ppm) to percent of chart was established for each multipoint calibration. The regression equation was applied to determine average hourly concentrations of pollutants from the strip chart readings.

All data were entered on SAROAD daily data forms in Tulsa. The data forms were mailed to RTI, checked, and then delivered, with strip charts, to EPA-EMSL for validation, keypunching, and printout in standard SAROAD format. All continuous data were handled in this way with the following exceptions: Beckman 6800 data (entered on SAROAD, validated by RTI, keypunched and printed by RTI); Tulsa Health Department WS/WD data (data obtained from Tulsa Health Department, printed by RTI); Tulsa ozone measurements at Mohawk and Apache locations (data received on magnetic tape from National Aerometric Data Bank). All of the continuous data are presented in Volume II of this report.

Table 3.3. Number and location of hydrocarbon samples collected in Tulsa, Oklahoma

Site or location	Morning 05 to 08 CST	Midmorning 08 to 11 CST	Afternoon 13 to 16 CST
Liberty Mounds	70	7	0
Health Department	77	7	1
Post Office	78	7	1
Sperry	10	7	5
Skiatook Lake	0	0	6
Vera	0	0	6
Wynona	0	0	5
Ochelata	0	0	5
Aircraft, upwind	24	0	0
Aircraft, over city	10	0	0
Aircraft, low pass	11	0	0
Aircraft, downwind	0	0	12

3.3 HYDROCARBON SPECIES SAMPLING PROGRAM

Approximately 235 integrated samples were taken during the 0600 to 0900 CDT period at three stations: Liberty Mounds, Tulsa Health Department, and Tulsa Post Office. An additional 114 samples were taken at other stations and aloft in different time frames during the period of airborne air quality measurements. Table 3.3 summarizes the number and location of hydrocarbon samples.

All samples were collected in 2-L stainless steel containers and shipped back to the Research Triangle Park for analysis by RTI. Details of the analysis procedure are given in Appendix A of this volume. Concentrations of individual species in each sample are compiled in Volume II of this report. Qualifying statements concerning the hydrocarbons data base are also given in Volume II.

3.4 TENAX GC/MS/COMP ANALYSES

Early in the program (July 10 and 11), field personnel collected two 24-hr samples on Tenax cartridges, one at Liberty Mounds and one at the Tulsa Post Office site. Later, on September 21, 3-hr samples were collected at the Liberty Mounds, Post Office, and Vera sites. All data and spectra associated with the GC/MS analyses are given in Volume II of this report.

3.4.1 Experimental Methods

The methods and procedures for the collection and analysis of volatile organics in ambient air are described in Appendix B of this volume. Briefly, organic vapors were collected using a solid sorbent, Tenax GC, in a cartridge by passing ambient air through the cartridge to trap the organic vapors. Subsequent analysis of the cartridges was performed by high resolution gas chromatography/mass spectrometry/computer for the separation and characterization of the organic species recovered from the Tenax GC cartridges.

Table 3.4 presents the ambient air GC/MS sampling protocol for volatile organics in Tulsa and vicinity. Essentially, five different samples were collected in duplicate on three different dates during the past summer. The first two samples were collected in July and represented sampling over a 24-hr period on two consecutive days at Liberty Mounds and the Post Office site in downtown Tulsa. The second set of samples was from Liberty Mounds, the Post Office site in downtown Tulsa, and Vera and represented volatile organics collected over a 3-hr period. In the latter set of samples, the objective was to compare the relative concentrations of volatile organics present in ambient air at the three sites.

The quantitation of chemical classes as well as individual species was performed on the GC/MS/COMP system utilizing the mass fragmentographic technique. The basic program calculates "area ratio," which is the area ratio of a selected ion to one specified ion (or the sum of specified ions) over a selected range of mass spectra. The program uses a subroutine for searching spectra that are stored on the fixed disk. The program prints out the "sum of ions" area, which is a specified ion or ions, and "selected ion area" as well as the area ratio and indicates saturated ion if an intensity is $\geq$32,736. This program was used to sum ion intensities representing chemical classes of compounds over a selected region of the chromatogram of the individual samples. The m/e 186 ion was the selected ion and is the sum of the intensities of the external standards perfluorobenzene and perfluorotoluene. The area measurements were of prime interest in this case, not the area ratios. Using this approach, it was possible to calculate the relative quantities of various chemical classes as well as individual species for the samples taken from Liberty Mounds, the Post Office in Tulsa, and Vera.

Table 3.4. Ambient Air Sampling Protocol for GC/MS/COMP Analysis of Volatile Organics

Sampling Site	Location	Code	Date	Period, CDT	Volume Sampled (L)
Liberty Mounds	District Water Works	LM1	7/10-11/77	0355-0355 hrs	160.8
Downtown Tulsa, OK	Post Office Garage Lot (2nd & Elwood)	DT1	7/11-12/77	0600-0600 hrs	142.5
Liberty Mounds	District Water Works	LM2	9/21/77	0600-0900 hrs	351
Downtown Tulsa, OK	Post Office Garage Lot (2nd & Elwood)	DT2	9/21/77	0600-0900 hrs	390
Vera	Vera Post Office	V1	9/21/77	1400-1700 hrs	390

Comparison among the three sites was made on a relative basis. The breakthrough volumes and sampling volumes were used to normalize the samples in arbitrary units per cubic meter of ambient air. The results obtained at these three sites are discussed in Chapter 6 of this volume and in Volume III, "Data Analysis and Interpretation."

SECTION 4.0

AIRBORNE AIR QUALITY MEASUREMENTS

4.1 MEASUREMENTS SYSTEM

A brief description of the airborne air quality measurements system is given in the following sections. A more detailed description of the system design was presented in a previous publication.[8]

4.1.1 Aircraft

The aircraft used in the program was a Piper Navajo B, shown in the photograph, Figure 4.1. The aircraft operates at a typical cruise speed of 280 km/hr (180 mph) which, with a normal crew complement (pilot and instrument operator) and instrumentation package, will allow an operational time of 3.5 hrs with 45 min of fuel reserve. The maximum operational altitude is 7,600 m (25,000 ft) with an initial climb rate capability exceeding 305 m/min (1000 ft/min). It is equipped with instrumentation for day and night VFR and IFR operations. Communications and navigation equipment include Dual VOR and VHF Communication, DME, ADV, Transponder, and an Altitude Reporting Altimeter.

4.1.2 Air Sampling System

A physical layout of the air sampling system is shown in Figure 4.2 and a functional layout of the system is shown in Figure 4.3. The air intake system consists of two 2.54-cm Teflon tubes inserted in steel tubes mounted to the nose cone of the aircraft and extending approximately 61 cm in front of the nose of the aircraft (see Figure 4.2). One of the Teflon probes terminates in an expansion manifold located in the nose compartment of the aircraft, supplying a clean air sample to an integrating nephelometer mounted in the nose compartment.

The second Teflon probe extends to the cabin area of the aircraft and attaches to a 12.7-cm diameter sample manifold, constructed of aluminum and coated internally with heat-cured Teflon. The manifold is designed with an inlet diverging diffuser section to allow deceleration of

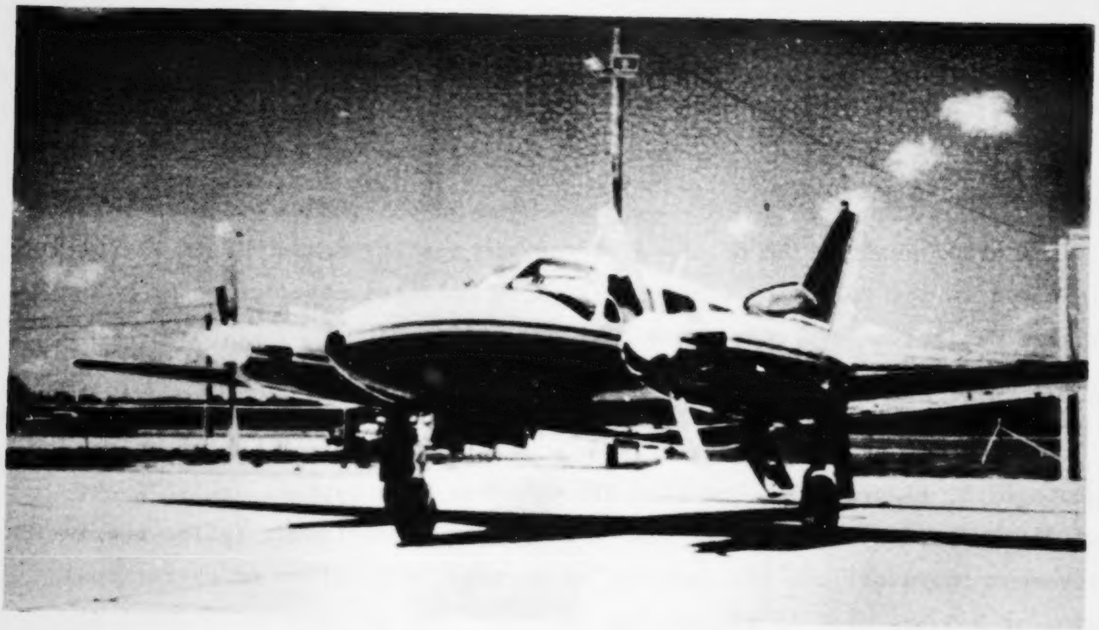


Figure 4.1. Instrumented aircraft.

flow to a more controllable velocity, typically in the range of 3 m/sec.

Analyzer sample lines, temperature, and dew point probes, etc. are situated along the main body of the manifold, an adequate distance from the diffuser, to allow unobstructed, isentropic flow of air sample. Manifold flow velocity, monitored with a hot wire anemometer, can be adjusted with an exit damper for variations in cabin pressure, altitude, and aircraft speed. A minimum flow velocity of 2-3 m/sec is maintained to insure relatively rapid air sample exchange. The manifold exhaust design includes a diverging diffuser section, minimizing the possibility of contamination from the aircraft cabin.

4.1.3 Instrumentation

Functional and equipment layouts for the aircraft instrumentation system used in this program are illustrated in Figures 4.4 and 4.5, respectively. The measured parameters are listed in Table 4.1, along with corresponding instrumentation, analysis technique, range of operation, and response time.

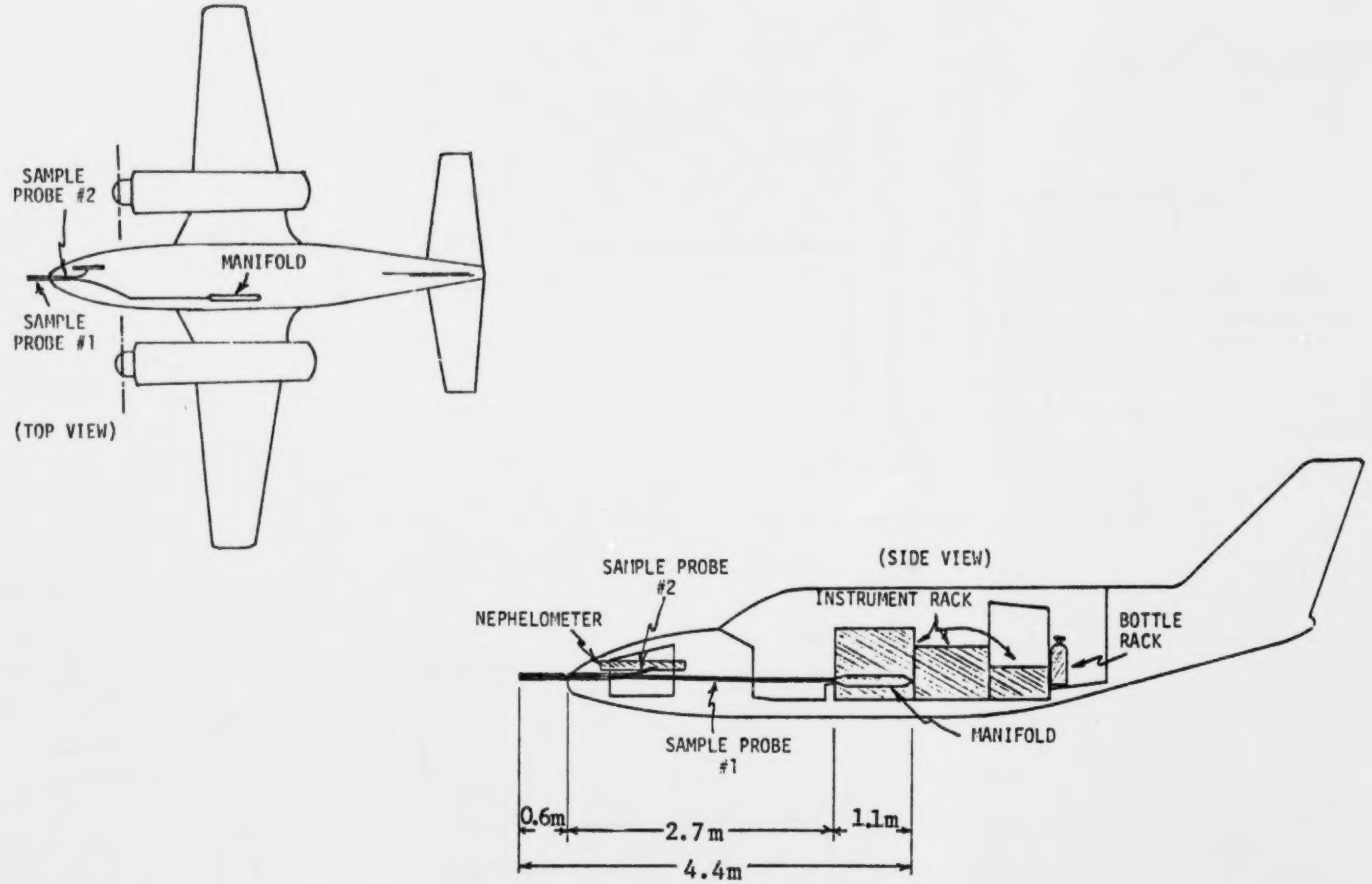

SAMPLE PROBE #2
MANIFOLD
SAMPLE PROBE #1
(TOP VIEW)
(SIDE VIEW)
SAMPLE PROBE #2
NEPHELOMETER
INSTRUMENT RACK
BOTTLE RACK
SAMPLE PROBE #1
MANIFOLD
0.6m
2.7m
1.1m
4.4m

Figure 4.2. Physical layout of air sampling system.

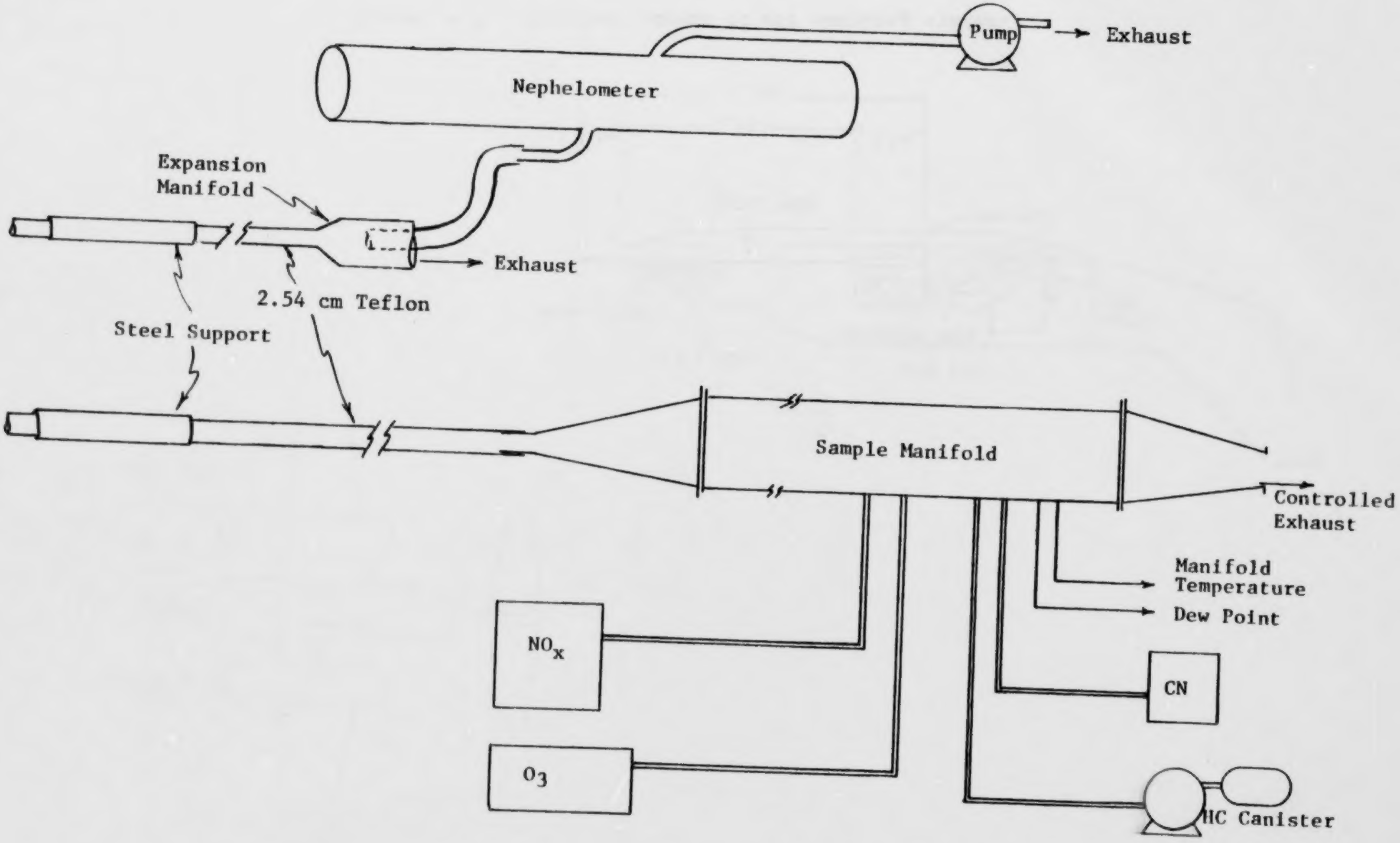

Pump
Exhaust
Nephelometer
Expansion Manifold
Exhaust
2.54 cm Teflon
Steel Support
Sample Manifold
Controlled Exhaust
Manifold Temperature
Dew Point
NO_x
CN
O_3
HC Canister

Figure 4.3. Functional layout of air sampling system.

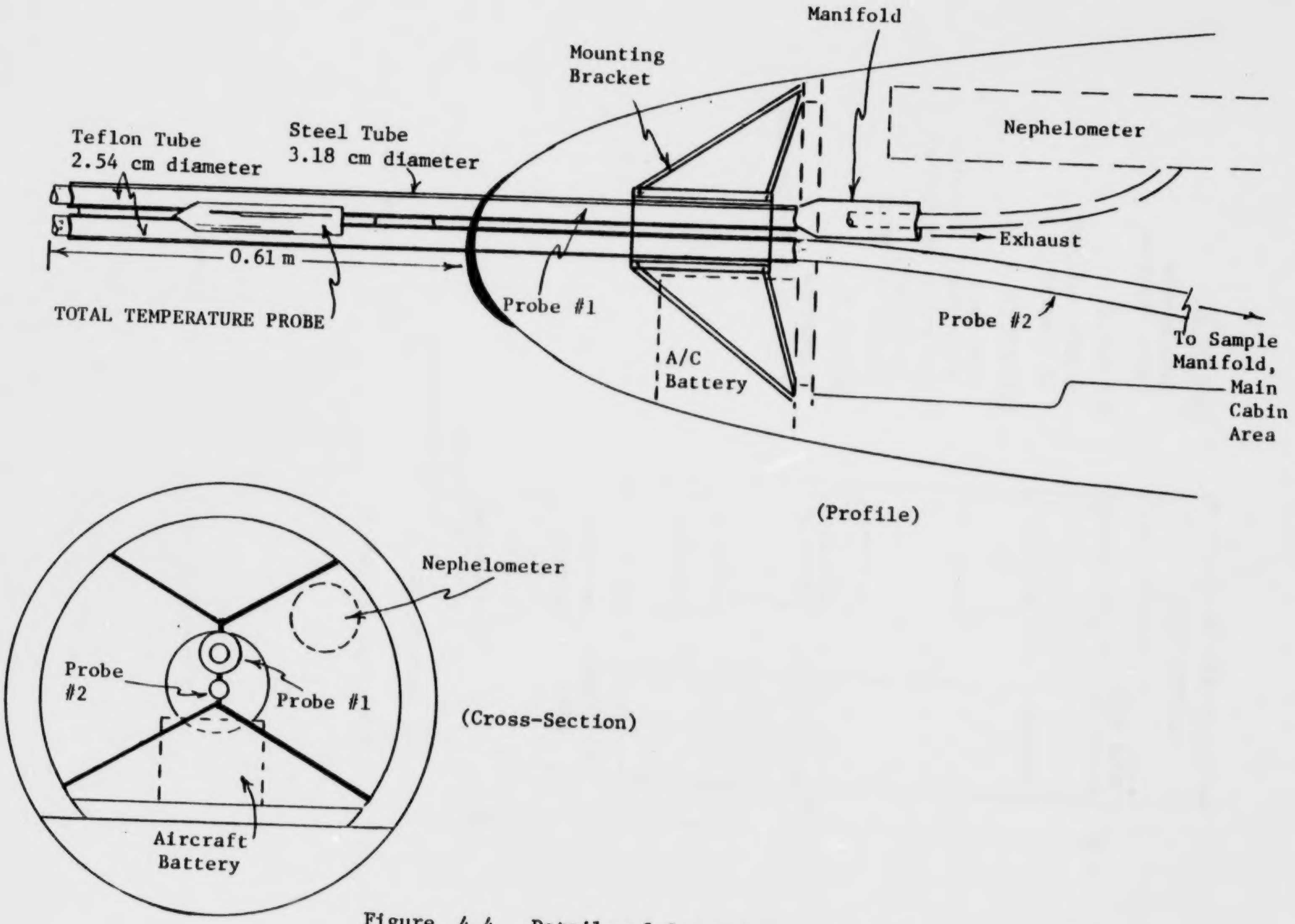
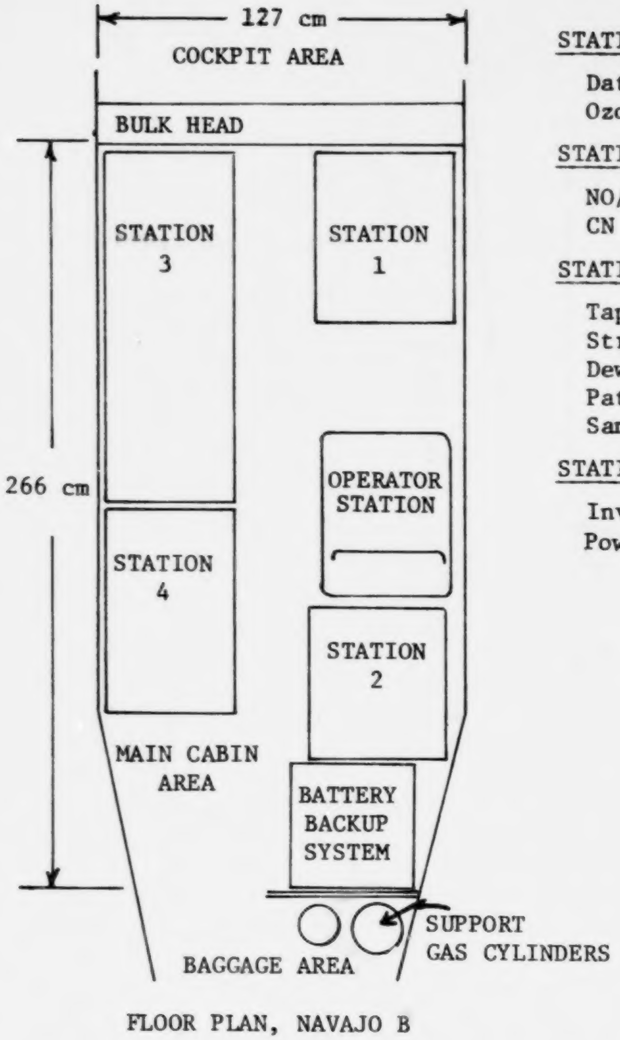

Manifold
Mounting Bracket
Teflon Tube 2.54 cm diameter
Steel Tube 3.18 cm diameter
Nephelometer
Exhaust
0.61 m
TOTAL TEMPERATURE PROBE
Probe #1
A/C Battery
Probe #2
To Sample Manifold, Main Cabin Area
(Profile)
Nephelometer
Probe #2
Probe #1
(Cross-Section)
Aircraft Battery

Figure 4.4. Details of forward section of air sampling system.


127 cm
COCKPIT AREA
BULK HEAD
266 cm
STATION 3
STATION 1
OPERATOR STATION
STATION 4
STATION 2
MAIN CABIN AREA
BATTERY BACKUP SYSTEM
SUPPORT GAS CYLINDERS
BAGGAGE AREA
FLOOR PLAN, NAVAJO B

STATION #1

- Data System
- Ozone Analyzer

STATION #2

- NO/NO_2 Analyzer
- CN Counter

STATION #3

- Tape Deck
- Strip Chart Recorders
- Dew Point/Temperature
- Patch Panel
- Sample Manifold

STATION #4

- Inverters
- Power Distribution Panel

Figure 4.5. Layout of aircraft system.

Table 4.1 Aircraft instrumentation

Parameter	Instrument Manufacturer and Model	Analysis/Collecting Technique	Measurement Range	Continuous	Time Response
Nitric Oxide and Nitrogen Dioxide	Monitor Labs 8440	Chemiluminescence	0-0.2 ppm	x	20 sec
Ozone	Bendix 8002	Chemiluminescence	0-0.2 ppm	x	5 sec
Hydrocarbons	RTI	Grab Samples - SS containers			2 min
Condensation Nuclei	Environment One Rich 100	Light Scattering	1,3,10,30,100, 300, 10Kx10^3 CN/CC*	x	5 sec
Light Scattering Coefficient (b_{scat})	MRI 1550B	Integrating Nephelometer	10,40,100x $10^{-4}m^{-1}$*	x	1 sec
Air Temperature	RTI	Bead Thermistor	-5 to +45°C	x	5 sec
Dew Point	EG&G 880	Cooled Mirror	-50° to +50°C	x	0.5 sec/°C
Altitude	Sensotec	Abs. Pressure Transducer	0 - 10,000 ft	x	1 sec
True Airspeed	Sensotec	Diff. Pressure Transducer	50 - 150 mph	x	1 sec
Location	King KX170B (206)	Aircraft VOR/DME	0-100 mi. from sta.	x	1 sec
Time of Day/Date	Monitor Labs DAS				1 scan/ 15 sec

*Available operating ranges

4.1.4 Data Acquisition System

The data acquisition system, shown in the overall system diagram, Figure 4.7, consisted of a Monitor Labs Data Logger, System 9400, a Cipher, Model 85H magnetic tape recorder, a signal coupler, and three Hewlett-Packard Model 680 strip chart recorders. Analog signals from the instruments were coupled to the data system through the signal coupler (junction box) that also housed all the necessary bridge circuits, scaling networks and voltage reference source. The analog signals were also available at a patch panel on the front of the signal coupler for purposes of maintenance and strip chart record selection. The panel included a simultaneous event marker and zero/span voltages for the three recorders and provided convenient access when checking instrument status with an external digital voltmeter.

The Monitor Labs data system included internal clock/control, a digital 18-column printer, a 20-digit manual data entry, and a 30-channel analog signal input capability.

Manual input data entries were used to indicate the operational status of the analyzers and instruments.

The Cipher tape transport system produced a computer-compatible, 1/2 in, 7-track magnetic tape with data storage density of 556 B.P.I.

4.2 INSTRUMENT CALIBRATION AND CHARACTERIZATION

4.2.1 Calibration Methods

Dynamic calibration techniques were used to calibrate and characterize analyzers and instrumentation, both in the laboratory prior to installation and in the field during the actual measurement program. Multipoint calibrations were conducted for the ozone and oxides of nitrogen analyzers prior to each flight day.

In addition, the ozone and oxides of nitrogen analyzers were audited by the Pedco, Corp. September 9, 1977. The results of this audit are reported in Section 5.3.2 of this report. Subsystems (pressure, temperature, etc.) were carefully calibrated at the beginning of the field measurement program and spot checked periodically throughout the measurement period.

Data were recorded on a digital magnetic tape data acquisition system. Information, such as position, events, and grab samples, was recorded via digit switches on the data system and/or log sheets. A digital printer was used for backup storages as well as observation of data in real-time and post-flight checks. In addition, three strip chart recorders were available for recording selected parameters in analog form.

The power system is so configured that equipment and/or subsystems requiring continuous power may be switched to battery power during periods when ground power is not immediately available. A battery supply, separate from the aircraft system, is provided for this purpose.

Ozone was measured with a Bendix Model 8002 gas phase chemiluminescent ozone analyzer, operated continuously on the 0-0.2 ppm range. C. P. grade ethylene support gas for the analyzer was supplied from a size 3A gas cylinder. The instrument exhaust was routed through plastic tubing and dumped overboard through a bulkhead panel, to the rear and underneath the aircraft.

Oxides of nitrogen were measured with a Monitor Labs gas phase chemiluminescent NO-NO_2-NO_x analyzer, Model 8440. The instrument was operated continuously on the 0-0.2 ppm range for both NO and NO_x simultaneously.

Condensation nuclei were measured with an Environment One, Model Rich 100, C.N. Counter. According to manufacturer specifications, the unit is capable of counting particles 0.0016 micron and larger in diameter, with a maximum concentration of 300×10^6 particles/cc and with a repeatability of ± 3 percent of full scale on all linear ranges.

Visibility (b_{scat}) was continuously measured with an integrating nephelometer, MRL model 1550B.

Environmental considerations of the air being sampled included temperature and dew point measurements inside the sample manifold and measurements of the adiabatic stagnation temperature of the air relative to the moving aircraft. Sample air temperature was measured with a YSI bead thermistor, Type 44202, mounted inside the sample manifold, downstream from the analyzer's sample lines. The sample dew point was continuously monitored with an EG&G, Model 880, dew point sensor. A YSI, Model 19, hygrometer was used to monitor the aircraft cabin air temperature and dew point. Ambient temperature measurements were made with a YSI bead thermister, Type 44202, mounted in a total temperature probe, positioned in front of the aircraft, mounted to the sample probe.

A Pitot tube, mounted underneath the aircraft wing, provided continuous measurement of the ambient static pressure, altitude, indicated airspeed and Mach number. The Pitot tube extended a sufficient distance below the wing's surface, minimizing measurement error caused by aerodynamic distortion from the aircraft.

Grab samples for subsequent hydrocarbon analysis were collected with the apparatus shown in Figure 4.6. Sample air was pumped from the manifold, through 0.64 cm o.d. stainless steel tubing with a single state stainless steel metal bellows pump. Samples were collected in an evacuated stainless steel canister, sealed with a bellows valve. The inlet to the canister was carefully purged for several minutes prior to opening the bellows valve and collecting the sample.

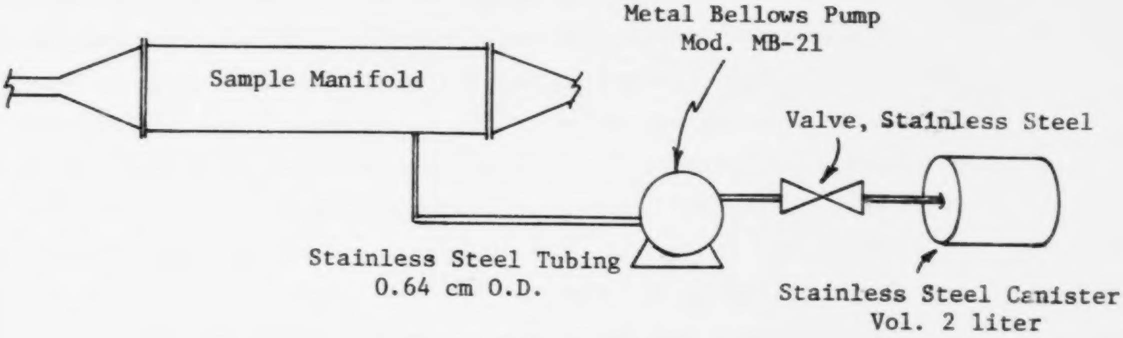

Metal Bellows Pump
Mod. MB-21
Sample Manifold
Valve, Stainless Steel
Stainless Steel Tubing
0.64 cm O.D.
Stainless Steel Canister
Vol. 2 liter

Figure 4.6. Hydrocarbon grab sample system.

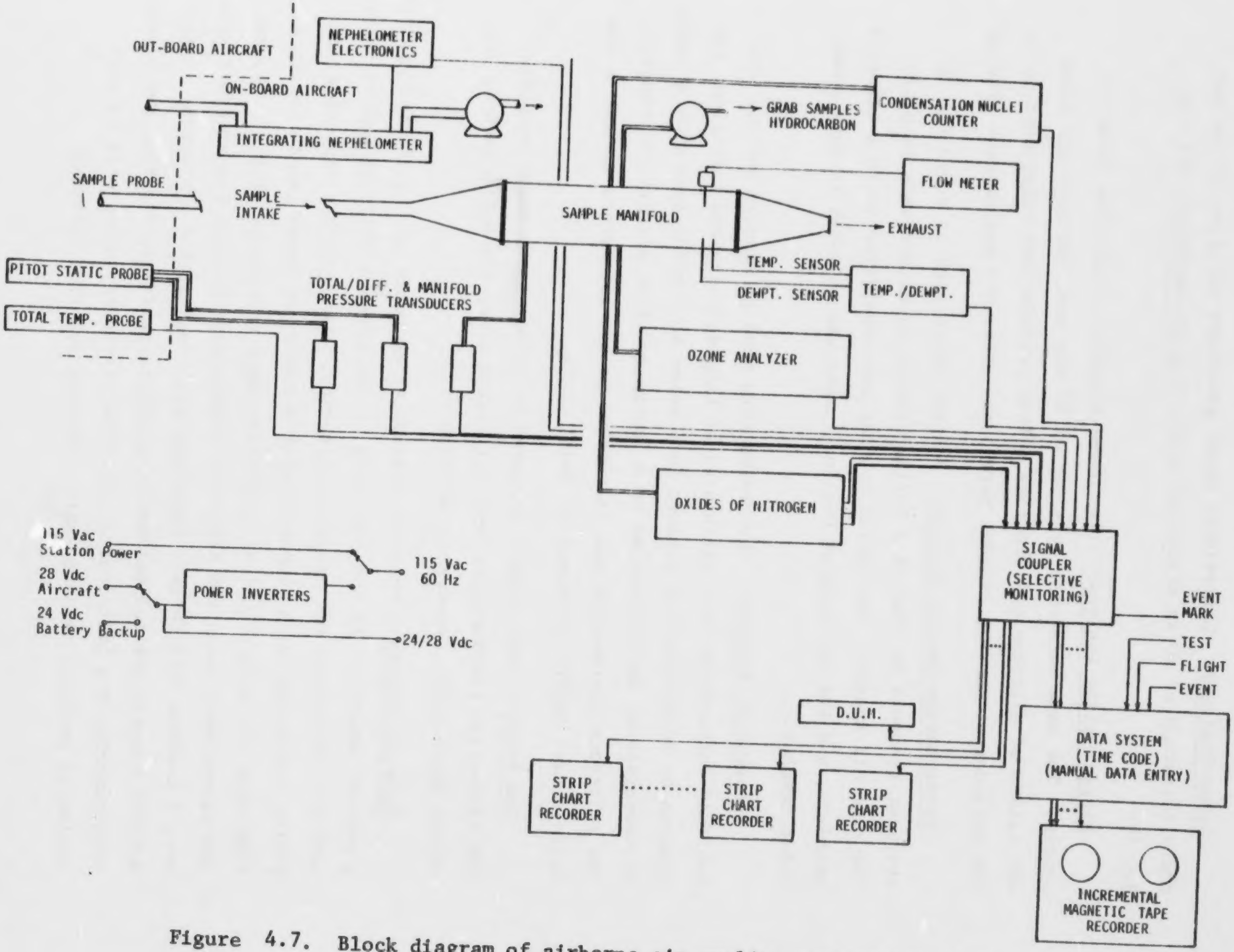

OUT-BOARD AIRCRAFT
ON-BOARD AIRCRAFT
NEPHELOMETER ELECTRONICS
INTEGRATING NEPHELOMETER
SAMPLE PROBE
SAMPLE INTAKE
SAMPLE MANIFOLD
GRAB SAMPLES HYDROCARBON
CONDENSATION NUCLEI COUNTER
FLOW METER
EXHAUST
TEMP. SENSOR
DEWPT. SENSOR
TEMP./DEWPT.
PITOT STATIC PROBE
TOTAL TEMP. PROBE
TOTAL/DIFF. & MANIFOLD PRESSURE TRANSDUCERS
OZONE ANALYZER
OXIDES OF NITROGEN
SIGNAL COUPLER (SELECTIVE MONITORING)
EVENT MARK
TEST
FLIGHT
EVENT
DATA SYSTEM (TIME CODE) (MANUAL DATA ENTRY)
D.U.M.
STRIP CHART RECORDER
STRIP CHART RECORDER
STRIP CHART RECORDER
INCREMENTAL MAGNETIC TAPE RECORDER
115 Vac Station Power
28 Vdc Aircraft
24 Vdc Battery Backup
POWER INVERTERS
115 Vac 60 Hz
24/28 Vdc

Figure 4.7. Block diagram of airborne air quality measurement system.

Ozone Analyzer: Ultraviolet ozone generator verified by the gas phase titration of NO as described in the Federal Register, Vol. 38, No. 10.

Nitric Oxides Analyzer: Gas phase dilution of NO with clean air source. The same reference cylinder of NO was used for both the ozone and oxides of nitrogen calibrations. This cylinder was referenced to an NBS cylinder of NO (NBS FF3193) before and after the measurement program.

Condensation Nuclei Counter: Factory calibrated by comparing instrument response to that of a Pollak Counter simultaneously sampling the same air source. The Pollak Counter was considered to be a suitable standard, and the Environment One instrument was adjusted to give comparable readout.

Temperature Sensors: The thermistors used to measure ambient and manifold temperature were calibrated at the beginning and throughout the program by submersing the sensors in a water bath maintained over a range of temperatures and referenced to a laboratory-type mercury thermometer. The reference thermometer was calibrated in the laboratory against a Hewlett-Packard quartz thermometer, Model 2801A.

Dew Point: Periodically compared to sling psychrometer readings. The respective thermometers were calibrated using the water bath as described above under temperature sensors.

Pressure System: Pressure transducer response was calibrated against a mercury manometer at the beginning of the program and spot-checked periodically throughout the measurement period. Also, in the beginning, repeated low passes were conducted over a runway of known length during a time when the meteorological conditions were reasonably stable. Several low passes were made from different directions, varying the aircraft speed over a maximum safe range. Each pass was timed with a stopwatch. Using airport temperature and barometric pressure readings, and time and distance measurements, the differential and total pressure sensor outputs were scaled to indicate ambient static pressure and true airspeed.

4.2.2 Pressure Effect Tests

In addition to routine characterization tests performed on the gas analyzers, the effects of changing altitude on instrument response were investigated. The experimental procedures for these tests are described in detail for earlier investigations of this type and are reported in Ref. 8.

The ozone and oxides of nitrogen analyzers used in the present program were characterized for pressure effect in May, 1977. The environmental test chamber facility at NERC, Las Vegas was used for the tests. The results of these tests produced a predictable decline in instrument response to a given concentration with increasing altitude (decreasing pressure) and are shown graphically in Figures 4.8 and 4.9 for ozone and NO_x analyzers, respectively.

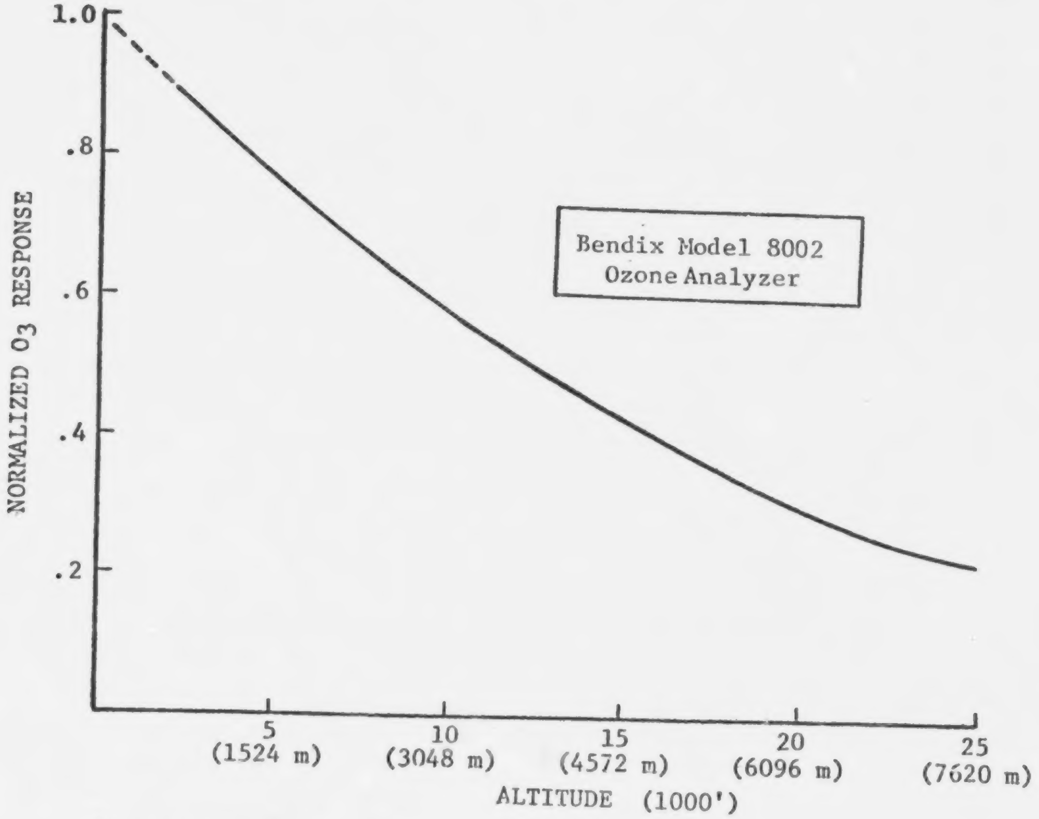


Figure 4.8 Ozone analyzer response (normalized to the analyzer's response at standard pressure) versus altitude.

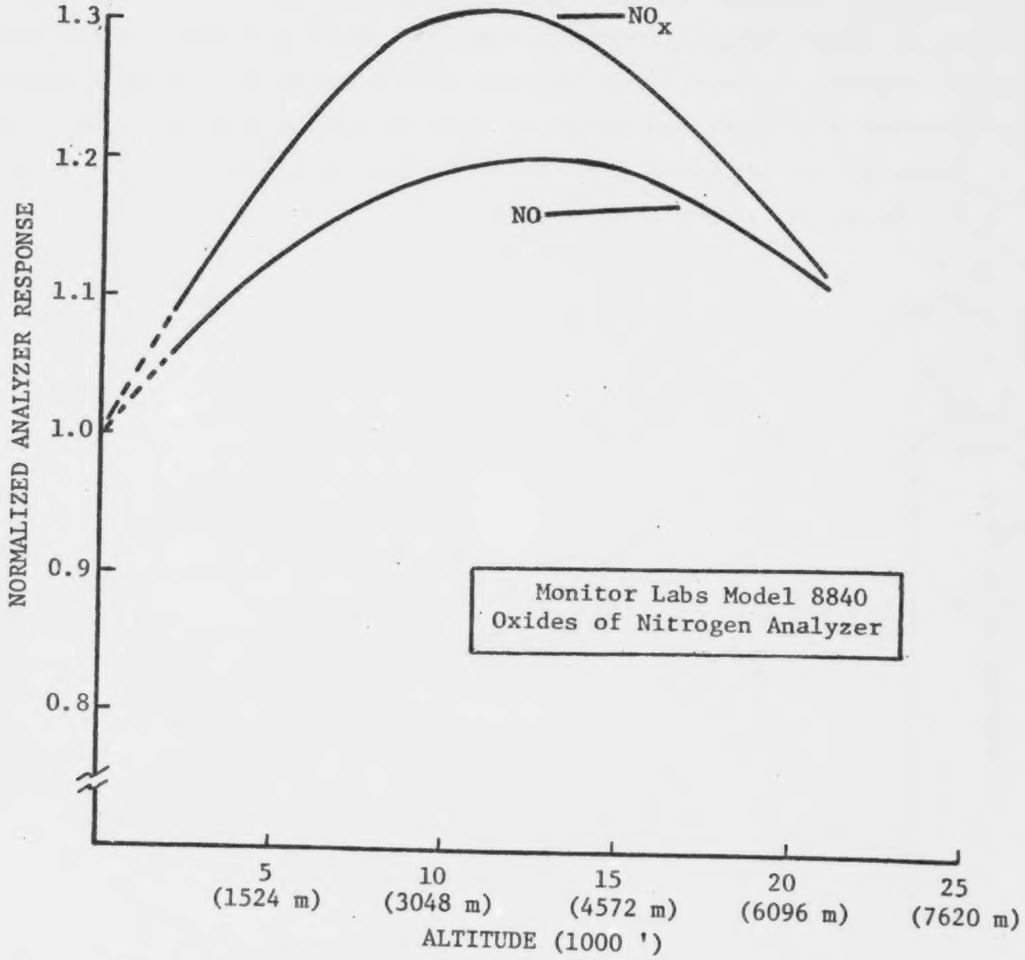


Figure 4.9. NO/NO_x analyzer response (normalized to the analyzers' response at standard pressure) versus altitude.

4.3 OPERATIONAL PROCEDURES

In order to insure uniform instrument operation and provide confidence in collected data beyond that established by the analyzer calibrations already described, specific operational and data validation procedures were routinely performed for each data flight.

The following preparations, procedures, and checklist requirements were performed immediately prior to each mission (pre-flight), during the mission (in-flight), and after completing the mission with the aircraft (post-flight). Actual readings were recorded on each checklist and in the general flight log for subsequent use, and instrument/analyzer test values or settings different from the normal were noted.

4.3.1 Pre-Flight Procedures

(1) Log observed weather, weather service report, and sling psychrometer readings on appropriate forms.

(2) Observe and inspect general condition of aircraft instrumentation and equipment, i.e., plumbing, air intake tubes, pitot-static probes, temperature probe, etc.

(3) Label hydrocarbon canisters for use during flight.

(4) Install clean Magnetic Tape Reel, replace strip chart recorder paper, and digital printer paper as required.

(5) Initiate DAS for several scans and observe active channels for any irregular readings. Observe strip chart records of overnight analyzer operation.

(6) Complete Pre-Flight Checklist (see Table 4.2).

(7) Review flight pattern with pilot prior to takeoff.

4.3.2 In-Flight Procedures

Initiate the following procedures and checklist after aircraft start-up (while on ramp) and immediately after lift-off.

(1) Switch inverters to A/C 28 Vdc.

(2) Reset DAS time, load magnetic tape, and time-mark strip chart recorders.

Table 4.2 Pre-flight checklist

Date ____________________
Time ____________________
Location ________________
Operator ________________
Flight No. ______________

O_3 ANALYZER
Range (0.2 ppm) __________
T.C. (10 sec.) ___________
Span Set ________________
Zero Set ________________
Total Flow (24) __________
C_2H_4 Press.(20) __________
Internal Zero ___________
Internal Span ___________

NO_x ANALYZER
Vacuum (25) ______________
Total Flow (Rot.) _________
NO Flow (Rot.) ___________
NO_x Flow (Rot.) __________
O_3 Flow (Rot.) ___________
Range (NO/NO_x) ___________
T.C. (NO/NO_x) ___________
Span Set (NO/NO_x) ________
Elect. Test (NO/NO_x) ______
Optic Test (NO/NO_x) _______
Oper. Mode ______________
Data Lamp _______________
Dessicant _______________

SUPPORT GASES
C_2H_4 Press. ______________
H_2 Press. ________________

CN COUNTER
Water Reservoir __________
Sample Flow _____________
Test Pos. _______________
Span (Low Range) _________
Oper. Range _____________

NEPHELOMETER
Flash Rate (8/sec) ________
T. C. (2 sec.) ___________
Oper. Mode ______________
Scale ___________________
Flash Lamp ______________

DEW POINT
Test and Balance _________
Oper. Mode ______________

STRIP CHART RECORDER
Select Parameter _________
Zero Set ________________
Span Set ________________
Time Mark and Label ______

D.A.S.
Manual Data Entry ________
Oper. Mode ______________

NOTE: Leave tape deck and DAS in standby mode until actual data measurements are to be made.

(3) Initiate several scans (DAS printout only) and review all channels for nominal values. Particularly review systems operating on 28 Vdc only, i.e., pressure transducer, turbulence, etc.

(4) Observe and complete In-Flight Checklist (see Table 4.3). The In-Flight Checklist is used immediately after lift-off and near the end of the flight.

(5) Throughout the flight, a general flight log was maintained by the operator, which included time, course, airspeed, altitude, climb/descent rate, position information, and local weather observations.

Table 4.3 In-flight checklist

Time ______________

Altitude ______________

POWER SYSTEM

A/C 28 Vdc ______________

Inverter Output #1 ______

#2 ______

#3 ______

#4 ______

#5 ______

#6 ______

O_3 ANALYZER

Total Flow ______________

C_2H_4 Flow (20) ______________

Oper. Mode ______________

NO_x ANALYZER

Vacuum (25) ______________

Total Flow (Rot.) ______________

NO Flow (Rot.) ______________

NO_x Flow (Rot.) ______________

O_3 Flow (Rot.) ______________

CN COUNTER

Range ______________

TURBULENCE

Low Test ______________

High Test ______________

Oper. Mode ______________

4.3.3 Post-Flight Procedures

With the conclusion of each flight and after aircraft refueling and maintenance, the entire instrumentation system (with the exception of grab sample pumps) was switched from backup battery power to a 115 Vac ground power source. The instruments aboard the aircraft were then repaired or adjusted as indicated by operational checks.

The data for the preceding flight were spot-checked and documented, and flight patterns were mapped with the appropriate time/position information. The data spot-checked consisted of reducing several representative data scans to engineering units and comparing these for realistic values.

4.4 DATA REDUCTION PROCESSING AND VALIDATION

The data from the RTI aircraft consists of a printer tape containing digitized voltage values from the sensors and gas analyzers located on board the aircraft. Before these data are analyzed, they must be processed to convert the voltage values to engineering units and apply corrections determined from known instrument altitude characteristics. In addition, some editing of the data must be done, such as the removal of data recorded during periods of instrument malfunction.

Due to the large volume of data and the repetitious nature of the calculations, the data were reduced on a computer, specifically the IBM 370 computer. Data from the data logger magnetic tape were dumped for a quick check on the data. Next, calibration equations were determined from the field analyzer calibration which was conducted nearest in time prior to each data flight. These equations for the gas analyzers were then compensated based on a known curve of instrument sensitivity change with altitude to determine the calibration equation for the analyzer when located at sea level.

The calibration equations and the raw voltage data were then input to the main computer processing program which accomplished the following functions:

- Computed temperature, altitude, from thermistor and pressure transducer voltage outputs.

- Computed gas concentrations from voltage values and calibration equations.
- Compensated computed gas concentrations for known changes in gas analyzer sensitivity with altitude.
- Removed or modified selected portions of data to correct for instrument malfunctions.
- Output data in a tabular format which facilitated comparison of data from different analyzers and allowed scanning of values from each analyzer or sensor.

The data from this program was inspected to determine which portions, if any, needed to be edited. Several means were available for establishing the reasonableness of the data including the following:

- Comparison of values between different parameters whose relative levels tend to be related.
- Comparison of successive values in one parameter for detection of outliers.
- Comparison of values from aircraft with those from ground station during periods when ground levels are likely to be near those at lower altitudes.

The computer-processing data validation-correction process is iterated until the data is correct. Then, a magnetic tape of data in engineering units is produced. This tape may be used for regenerating reports, further computer analysis or dissemination of the data. The format of this 9-track tape is shown in Figure 4.10 and the format of each record is shown in Table 4.4.

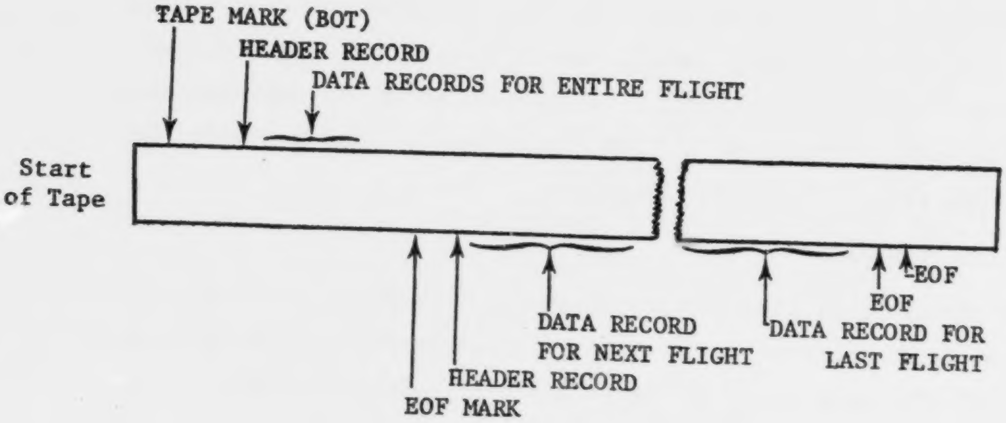

TAPE MARK (BOT)
HEADER RECORD
DATA RECORDS FOR ENTIRE FLIGHT
Start of Tape
EOF
EOF
DATA RECORD FOR NEXT FLIGHT
DATA RECORD FOR LAST FLIGHT
HEADER RECORD
EOF MARK

Figure 4.10. Format of magnetic tape.

Table 4.4. Format of header records and data records

FIELD NO.	FORTRAN FORMAT	HEADER RECORD	DATA RECORD
1st	F6.1	FLAG=8888.8	FLAG=9999.9
2nd	F6.1	FLIGHT NUMBER	LEG IDENTIFICATION NUMBER
3rd	F6.1	JULIAN DATE	HOUR
4th	F6.1	MONTH	MIN } OF DATA POINT
5th	F6.1	DAY	SEC
6th	F6.3	YEAR	OZONE (ppm)
7th	F6.3	TIMECODE 0=MORNING 1=AFTERNOON	NO (ppm)
8th	F6.3	0.0	NO_x (ppm)
9th	F6.1	0.0	b_{scat} (10^{-4}/m)
10th	F6.1	0.0	CN (1000/cc)
11th	F6.1	0.0	Dew Point (°C)
12th	F6.1	0.0	Temp. (°C)
13th	F6.0	0.0	Altitude (feet)

On the tape, each record is 78 characters long and is composed of 13 fields each 6 characters in length. Each flight is separated by an end-of-file (EOF) mark, and the last flight's data is followed by two EOF marks to signal end of volume. The tape is generated on a 9-track machine using IBM's standard EBCDIC code. The data is unblocked on a non-labeled tape. Other important information about the tape includes: the logical record length is 78, the block size is 78, the density is 800 bpi, and record format is fixed.

4.5 FLIGHT PROGRAM

The objective of the flight program was to measure selected pollutant and meteorological parameters aloft from an airborne platform in support of the 1977 EPA ozone study in the vicinity of Tulsa, Oklahoma.

4.5.1 Flight Protocol

Flight patterns and their relative priority were established in coordination with the EPA Project Officer prior to the field program. The decision was made to fly four days of transport patterns (preferably with two consecutive days in a set) as number one priority, and to fly the stagnation pattern with one flight day as second order of priority. A mid-day vertical spiral south of the city and an open box flight pattern around a power plant were set as possible alternatives if weather conditions, time, etc. permitted. The types of flight patterns to be flown on a particular day were determined on a day-by-day basis by the Project Officer who had access to real-time ground station oxidant data and meteorological forecasts for the area. Final flight determinations were made by the aircraft crew based on immediate meteorological conditions and equipment status.

The transport and stagnation patterns are described as follows:

Transport Pattern (To be flown when predicted wind speeds are 6-10 knots out of the south, and maximum daily O_3 concentration is expected to be 0.1 ppm or higher.)

AM Flight Plan

Purpose: Determine concentrations of ozone and other pollutants coming into the Tulsa area from the south.

Procedure:

- Make low pass over MOUNDS site at 0630 LDT (½ hour before sunrise). Take HC grab sample on low pass.
- Spiral up over MOUNDS site to 10,000 ft (3048 m). Take HC grab samples at 2500 ft (762 m), 5000 ft (1524 m), and 7500 ft (2286m).
- Descend to an altitude of 2500-3000 ft MSL 36 km (22.5 miles) W of MOUNDS and make W-E flight over MOUNDS site, total flight path 72 km (45 miles).
- Continue open box or square wave pattern toward Tulsa (as shown on map-designated to allow for completion of sprial and arrival at Tulsa International Airport at 0900 LDT).

- Begin spiral just N of Central Business District and ascend to 10,000 ft MSL. HC Grab Sample at 2500 ft and 7500 ft MSL.
- Make low pass at 0900 LDT at Tulsa International (TUL) Airport. HC Grab Sample on low pass.
- Make low pass at Downtown Airport. HC Grab Sample on low pass.

PM Flight Plan

Purpose: Determine the distributions and maximum concentrations of ozone, etc. downwind of the city as measured aloft.

Procedure:

- Begin 145 km (90-mile) W-E flight at 2500-3000 ft (MSL) 72 km (45 miles) due E of SPERRY site, at approximately 1230 LDT. Purpose of first leg is to identify edges of plume via b_{scat}, CN and/or O_3 with strip chart recordings.
- Open box or square wave pattern continued to the North with E-W legs shortened to allow greater northern progression in pattern for a given period of time. Adjust open box to allow for start of spiral in O_3 max area at approximately 1500 LDT. Purpose of this set is to identify the approximate location of the O_3 maximum in the Tulsa plume.
- Spiral to 12,000 ft in the area estimated to contain the maximum O_3 concentration. HC Grab Sample at 2500 ft and 7500 ft MSL.

Stagnation Pattern (To be flown when wind speed is predicted to be less than 5 knots, and maximum daily O_3 concentration is expected to be 0.1 ppm or higher.)

AM Flight Plan

Purpose: Determine O_3 and O_3 precursor distributions over and near the city on a day with light and variable winds.

Procedure:

- Fly a box pattern approximately 39 km (24 miles) on a side, at 2500 ft MSL. Start pattern at approximately 0630 LDT. (Set pattern uniformly on city.)
- Fly outer box pattern approximately 77 km (48 miles) on a side at 2500 ft MSL.
- Low passes at Riverside and Downtown Airport. Take HC Grab Sample at each site.

PM Flight Plan

Purpose: Determine O_3 and O_3 precursor distributions over and near the city at the expected time of maximum ozone concentration.

Procedure:

- Fly inner box pattern starting at approximately 1300 LDT. (Let drift with winds, keeping city inside inner box.)
- Fly outer box pattern.
- 2 spirals to 12,000 ft MSL inside inner box at approximate upwind and downwind locations. HC Grab Sample at 2500 ft, 5000 ft and 7500 ft MSL on each spiral.

4.5.2 Flight Summary

Data flights were conducted in the Tulsa area during the period August 25, 1977 through September 17, 1977. A summary of the flights conducted, data acquisition start and finish times, and the type of flight patterns are given in Table 4.5.

Flight T09 (morning) and Flight T10 (afternoon) shown in Figure 4.11 illustrate a typical transport flight pattern.

4.6 AIRCRAFT DATA

All aircraft data have been processed, validated, and entered in computer-compatible format on magnetic tape. A complete set of computer printouts of all of the data is included in Volume II of this report. A log of hydrocarbon grab samples taken which have been analyzed and validated is given in Table 4.6. A tabulation of low pass flights is given in Table 4.7, which presents the flight number, date, time, location, and ozone level recorded.

An example of the airborne data during the September 2, 1977 AM and PM transport flights shown in Figure 4.11 includes the following: ozone data plot for horizontal traverses (oxides of nitrogen are not included since concentrations were consistantly at or below the minimum detectable limit of the analyzer), Figure 4.12; temperature/dew point data plot for horizontal traverses, Figs. 4.13-4.14; b_{scat} data plot for horizontal traverses, Fig. 4.15; data plots of ozone, oxides of nitrogen, temperature, dew point, b_{scat} and condensation nuclei for two AM spirals and one PM spiral, Figures 4.16, 4.17, and 4.18, respectively. In addition, an example computer printout data sheet for the September 2, 1977 flights is given in Table 4.8.

Table 4.5
Tulsa Aircraft Measurement
Data Flights Summary

Flight Number	Date (1977)	Flight Time[1] (CST) Start	Finish	Type of Flight
T-03	25 Aug.	0813	0922	AM Transport[2]
T-04		1324	1417	PM Transport[2]
T-05	26 Aug.	0522	0746	AM Transport
T-06		1153	1415	PM Transport
T-09	2 Sept.	0530	0801	AM Transport
T-10	2 Sept.	1224	1436	PM Transport
T-11	3 Sept.	0527	0747	AM Transport
T-12	3 Sept.	1232	1440	PM Transport
T-14	8 Sept.	1152	1223	AM Stagnation[3]
T-15	9 Sept.	1402	1553	PM Transport
T-16	11 Sept.	0524	0730	AM Transport
T-17	16 Sept.	0526	0709	AM Transport
T-18	16 Sept.	1237	1424	PM Transport
T-19	17 Sept.	0539	0742	AM Transport
T-20	17 Sept.	1237	1427	PM Transport

[1] Spirals and horizontal flight times, inclusive; does not include low passes.

[2] No spirals or HC samples.

[3] Inner box only.

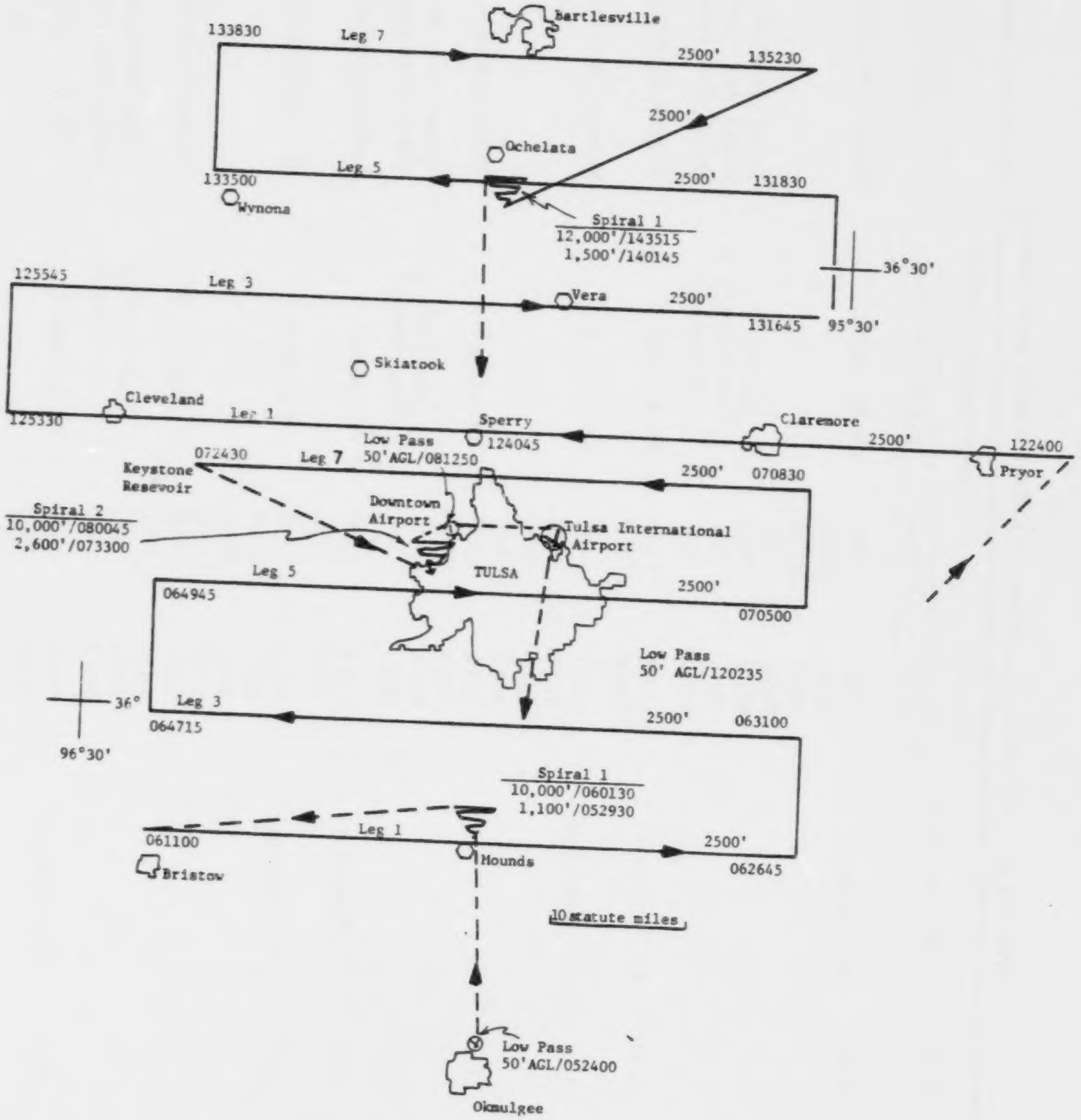

Bartlesville
133830
Leg 7
2500'
135230
2500'
Ochelata
Leg 5
133500
2500'
131830
Wynona
Spiral 1
12,000'/143515
1,500'/140145
36°30'
125545
Leg 3
Vera
2500'
131645
95°30'
Skiatook
Cleveland
125330
Leg 1
Sperry
124045
Claremore
2500'
122400
Pryor
Low Pass
50'AGL/081250
072430
Leg 7
2500'
070830
Keystone
Resevoir
Spiral 2
10,000'/080045
2,600'/073300
Downtown
Airport
Tulsa International
Airport
TULSA
Leg 5
064945
2500'
070500
Low Pass
50' AGL/120235
36°
Leg 3
064715
96°30'
2500'
063100
Spiral 1
10,000'/060130
1,100'/052930
Leg 1
061100
2500'
062645
Bristow
Mounds
10 statute miles
Low Pass
50'AGL/052400
Okmulgee

Fig. 4.11. Typical transport flight pattern.

Table 4.6. Aircraft log sheet - hydrocarbons grab samples

Flight Number	Date (1977)	Flight Pattern	HYDROCARBON SAMPLE			
			ID #	Altitude	Spiral/Low Pass	Location
T-05	8/26	AM Transport	9001	1200	AM Spiral 1	Mounds Monitoring Site
			9002	2500		
			9003	5000		
			9004	7550		
			9005	2500	Spiral 2	Tulsa Central Bus. District
			9006	725	Low Pass 1	Tulsa Int. Airport
			9007	775	Low Pass 2	Tulsa Downtown Airport
T-06	8/26	PM Transport	9008	2500	PM Spiral 1	Sperry Monitoring Site
			9009	7500		
T-09	9/2	AM Transport	9010	1100	AM Spiral 1	Mounds Monitoring Site
			9011	2600		
			9012	5000		
			9013	7600		
			9014	2600	AM Spiral 2	Tulsa Central Bus. District
			9015	7500		
			9016	725	Low Pass 1	Tulsa Int. Airport
			9017	775	Low Pass 2	Tulsa Downtown Airport
T-10	9/2	PM Transport	9018	2500	PM Spiral 1	Ramona, Oklahoma
			9019	7500		
T-11	9/3	AM Transport	9020	1250	AM Spiral 1	Mounds Monitoring Site
			9021	2500		
			9022	5000		
			9023	7700		
			9024	2500	Spiral 2	Tulsa Central Bus. District
			9025	7500		
			9026	775	Low Pass 1	Tulsa Downtown Airport
			9027	725	Low Pass 2	Tulsa Int. Airport
T-12	9/3	PM Transport	9028	2500	PM Spiral 1	5 mi E of Ramona, Okla.
			9029	7500		

Table 4.6. Aircraft log sheet - hydrocarbon grab samples (continued)

Flight Number	Date (1977)	Flight Pattern	HYDROCARBON SAMPLE			
			ID #	Altitude	Spiral/Low Pass	Location
T-15	9/8	PM Transport	9030	2600	PM Spiral 1	Ramona, Oklahoma
			9031	7550		
T-16	9/11	AM Transport	9032	1500	AM Spiral 1	Mounds Monitoring Site
			9033	2500		
			9034	5000		
			9035	7500		
			9036	2500	AM Spiral 2	Tulsa Central Bus. District
			9037	7800		
			9038	725	Low Pass 1	Tulsa Int. Airport
T-17	9/16	AM Transport	9039	1500	AM Spiral 1	Mounds Monitoring Site
			9040	2700		
			9041	5000		
			9042	7500		
			9043	2500	Spiral 2	Tulsa Central Bus. District
			9044	775	Low Pass 1	Tulsa Downtown Airport
			9045	725	Low Pass 2	
T-18	9/16	PM Transport	9046	2500	PM Spiral 1	Talala, Oklahoma
			9047	7500		
T-19	9/17	AM Transport	9048	1500	AM Spiral 1	Mounds Monitoring Site
			9049	2500		
			9050	5000		
			9051	7500		
			9052	2500	Spiral 2	Tulsa Central Bus. District
			9053	7500		
			9054	775	Low Pass 1	Tulsa Downtown Airport
			9055	725	Low Pass 2	Tulsa Int. Airport
T-20	9/17	PM Transport	9056	2500	PM Spiral 1	Nowata, Oklahoma
			9057	7600		

Table 4.7. Low pass data (ozone)

Flight Number	Date (1977)	Time (CST)	Location	Ozone (ppm)
T-05	8/26	0803	International Airport	0.057
		0835	Downtown Airport	0.049
T-09	9/2	0524	Okmulgee	0.037
		0813	International Airport	0.020
		0817	Downtown Airport	0.038
T-10	9/2	1203	Okmulgee	0.068
T-11	9/3	0523	Okmulgee	0.019
		0758	International Airport	0.030
		0802	Downtown Airport	0.037
T-12	9/3	1210	Okmulgee	0.090
T-14	9/8	1137	Okmulgee	0.073
T-15	9/8	1439	Okmulgee	0.063
T-16	9/11	0518	Okmulgee	0.029
		0739	International Airport	0.028
T-17	9/16	0521	Okmulgee	0.039
		0715	Downtown Airport	0.014
		0719	International Airport	0.008
T-19	9/17	0535	Okmulgee	0.045
		0754	Downtown Airport	0.039
		0758	International Airport	0.039
T-20	9/17	1215	Okmulgee	0.056

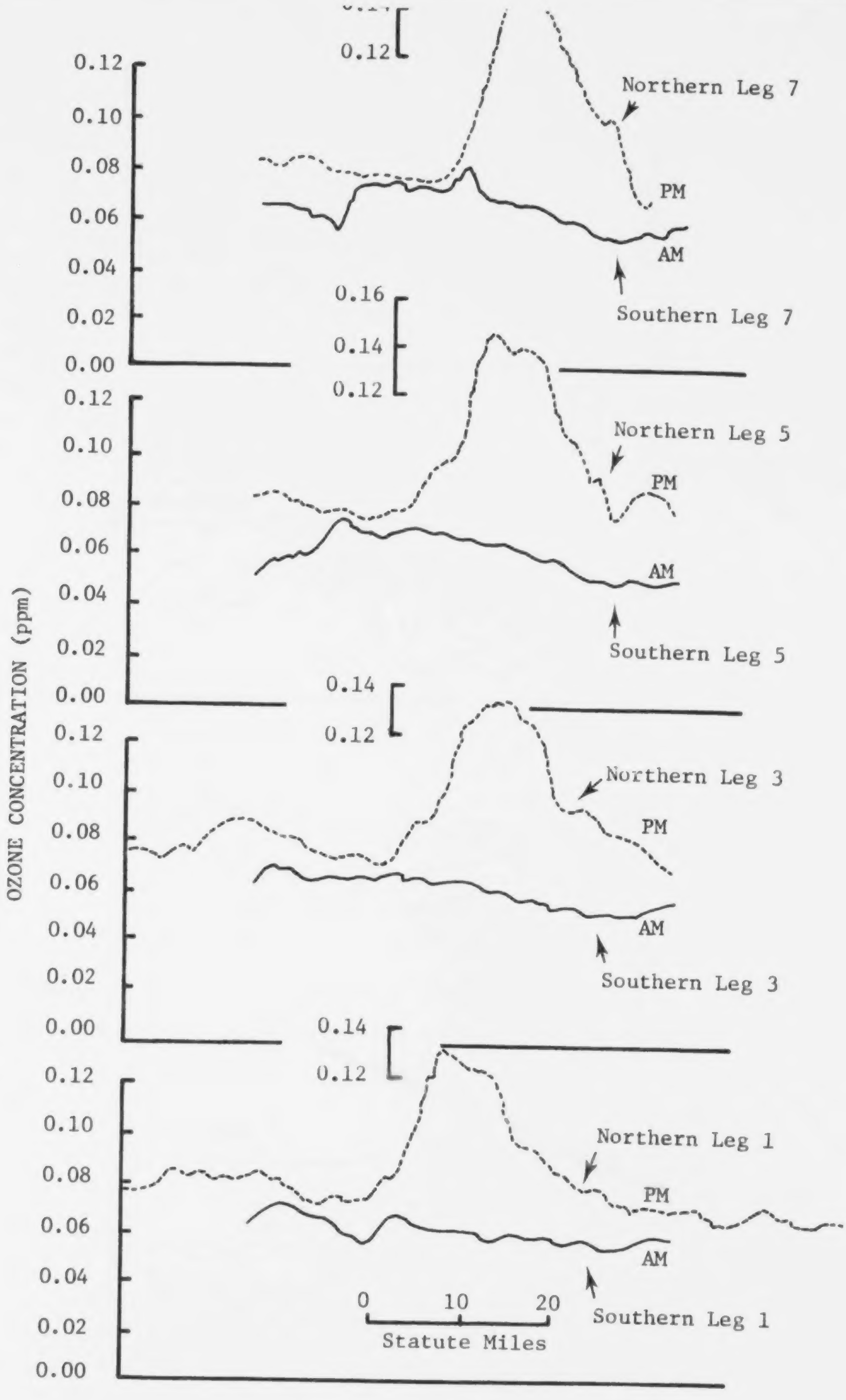


Fig. 4.12. O_3 for horizontal tracks - flights T09 and T10.

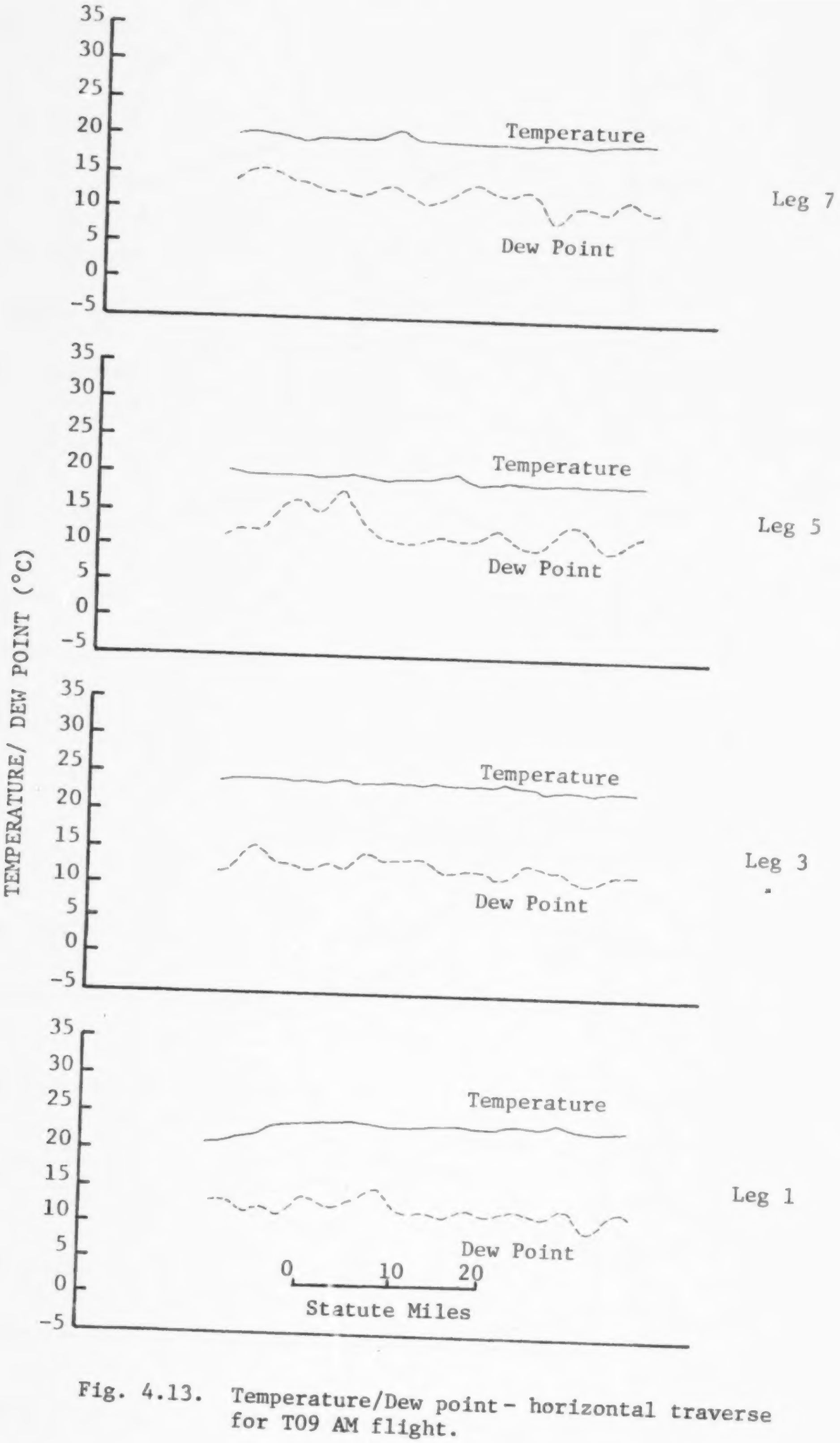


Fig. 4.13. Temperature/Dew point - horizontal traverse for T09 AM flight.

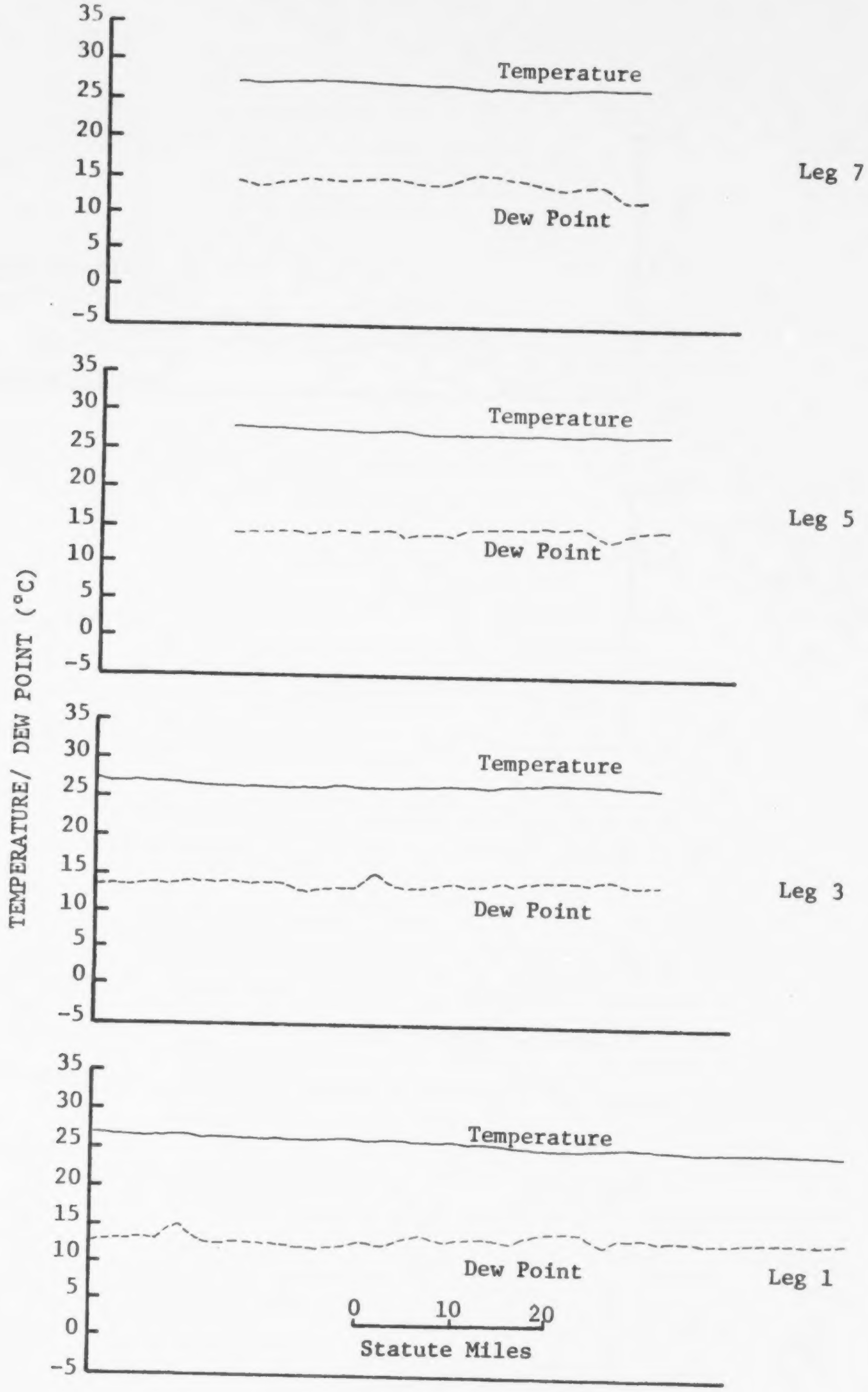


Fig. 4.14. Temperature/Dew point - horizontal traverse for T10 PM flight.

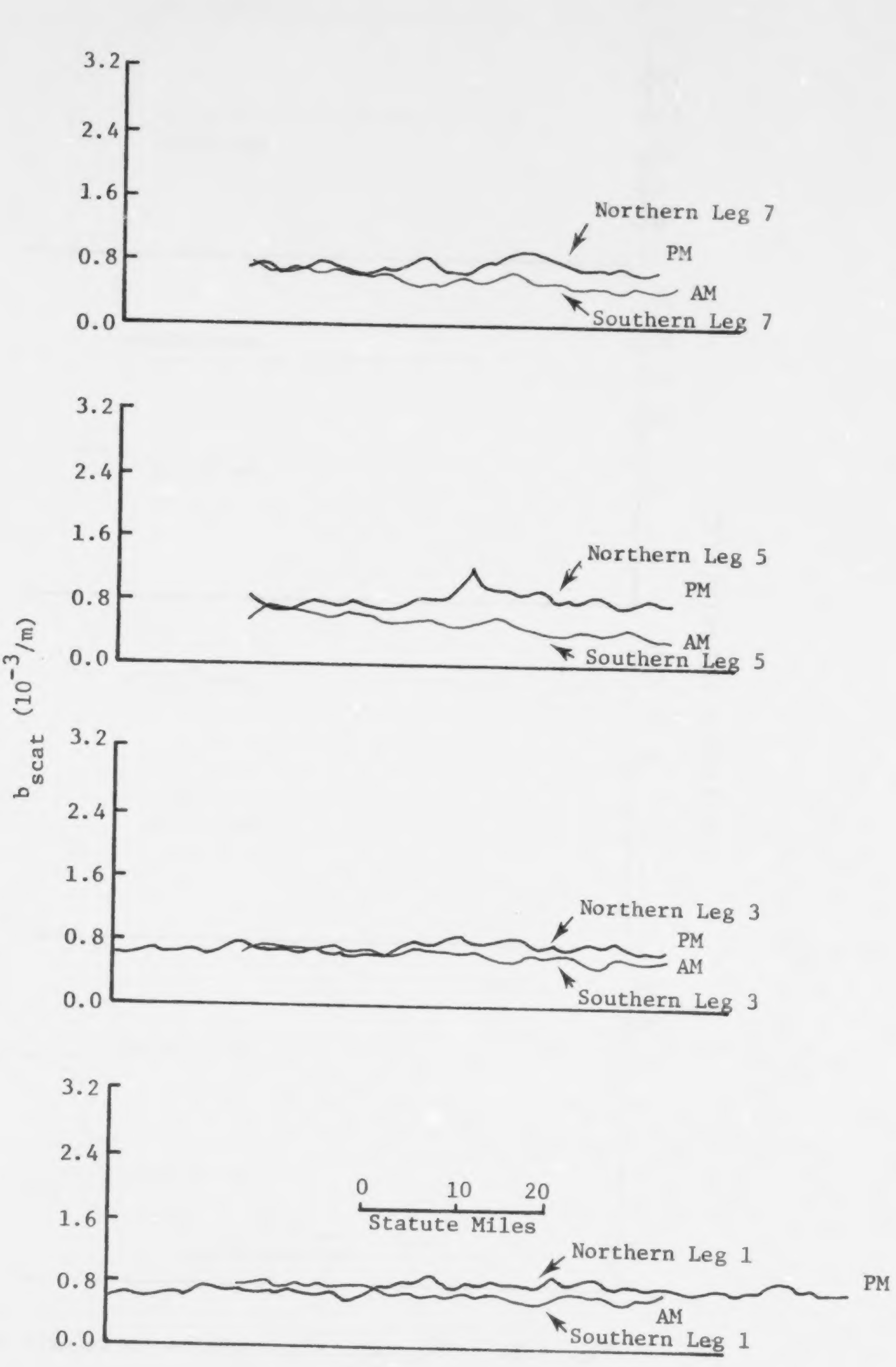


Fig. 4.15. b_{scat} for horizontal tracks - flights T09 and T10.

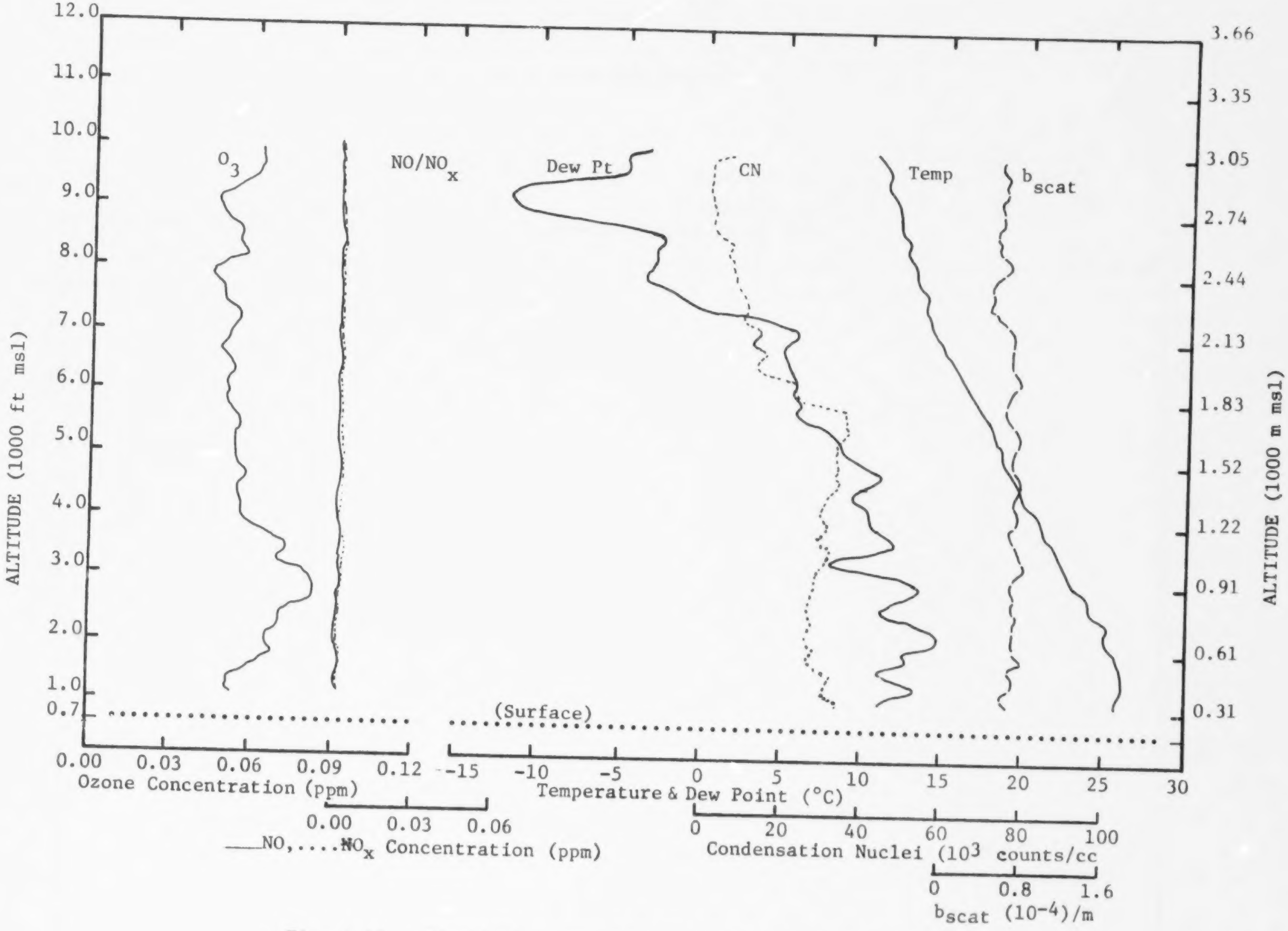


Fig. 4.16. AM spiral 1 over Liberty Mounds, flight T09.

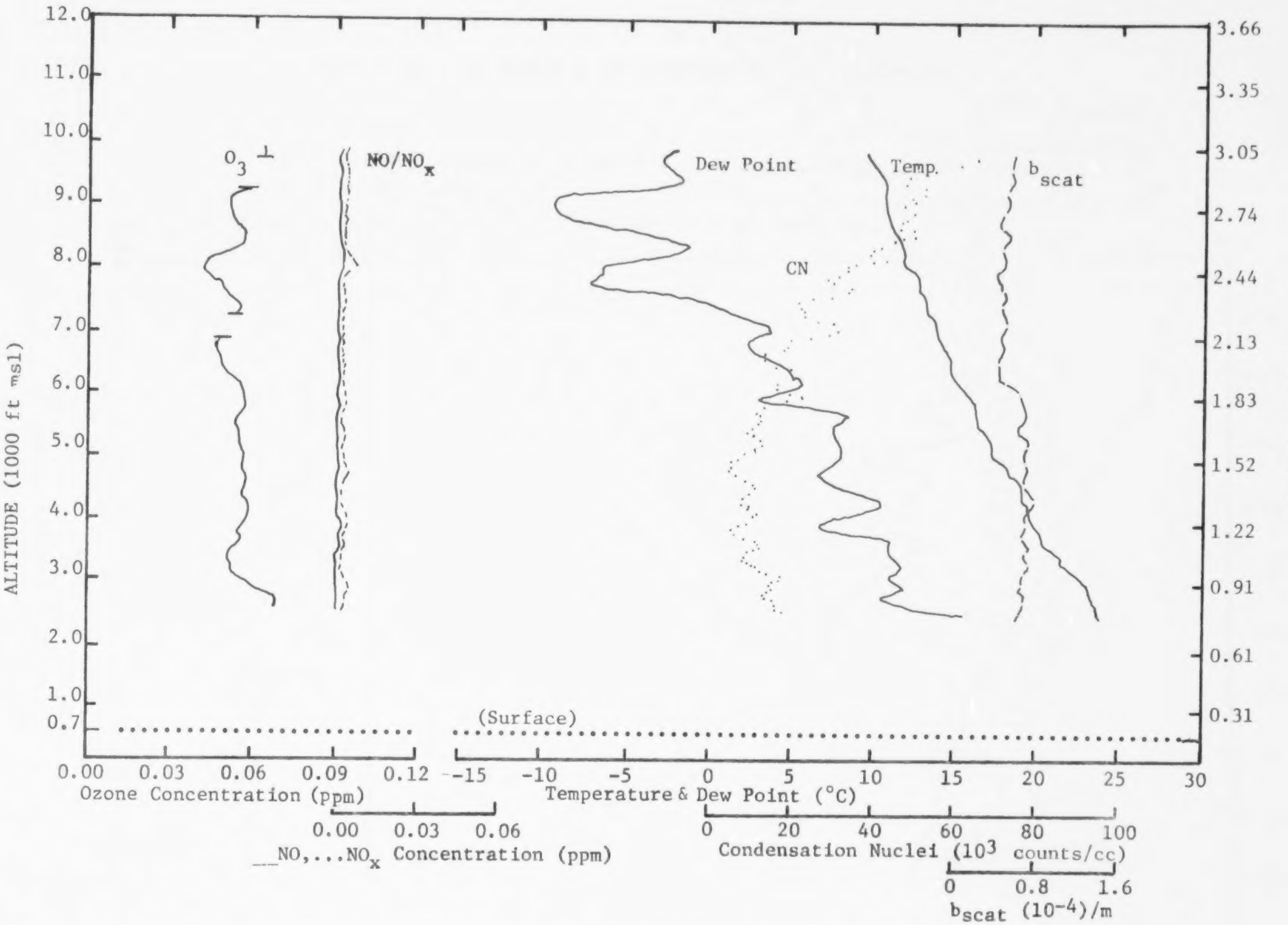


Fig. 4.17. AM spiral 2 over downtown Tulsa, flight T09.

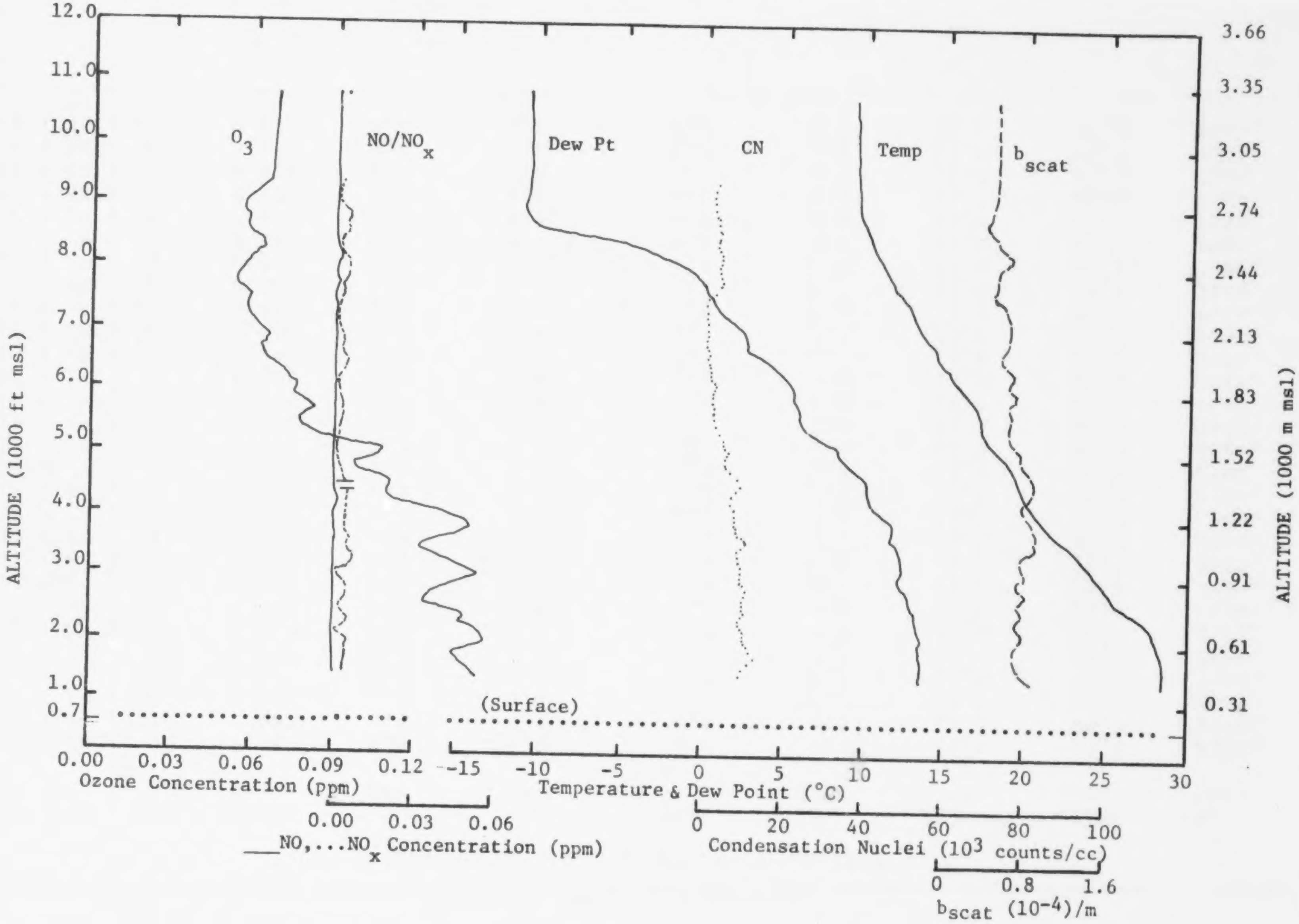


Fig. 4.18. PM spiral 1 over Ochelata, flight T10.

Table 4.8. Sample data printout

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                         TULSA FLIGHT NUMBER 10      DATE:  9- 2- 1977
LEG   HR  MIN   SEC    OZONE      NO       NOX      B-SCAT      CN       DEW PT    TEMP     ALT
                        PPM      PPM       PPM     .0001/M   1000/CC      °C        °C      FEET

  1   12 : 24 :  0     0.064     0.0      0.002       0.8       0.7       13.9      25.7    2580.
  1   12 : 24 : 15     0.067     0.0      0.0         0.8       0.3       13.7      25.9    2570.
  1   12 : 24 : 30     0.066     0.0      0.0         0.7       3.2       13.7      25.8    2560.
  1   12 : 24 : 45     0.070     0.0      0.003       0.8       0.5       13.9      25.8    2580.
  1   12 : 25 :  0     0.067     0.0      0.0         0.8       1.7       13.7      25.7    2590.
  1   12 : 25 : 15     0.063     0.0      0.0         0.9       0.9       13.5      25.9    2580.
  1   12 : 25 : 30     0.061     0.0      0.0         0.7       0.8       13.4      25.9    2680.
  1   12 : 25 : 45     0.067     0.0      0.007       0.8       0.9       13.5      25.9    2580.
  1   12 : 26 :  0     0.066     0.0      0.0         0.9       0.4       13.5      25.8    2600.
  1   12 : 26 : 15     0.071     0.0      0.004       1.0       2.3       13.6      25.9    2560.
  1   12 : 26 : 30     0.069     0.0      0.002       0.9       1.8       13.7      25.8    2580.
  1   12 : 26 : 45     0.063     0.0      0.002       1.0       1.6       13.7      25.8    2580.
  1   12 : 27 :  0     0.079     0.0      0.007       0.9       1.7       13.7      25.8    2580.
  1   12 : 27 : 15     0.072     0.004    0.004       0.7       1.4       13.7      25.9    2570.
  1   12 : 27 : 30     0.072     0.0      0.0         0.9       2.4       13.6      25.7    2580.
  1   12 : 27 : 45     0.070     0.0      0.0         0.8       1.0       13.7      25.9    2580.
  1   12 : 28 :  0     0.068     0.0      0.0         0.8       1.5       13.7      25.6    2600.
  1   12 : 28 : 15     0.069     0.0      0.0         0.7       1.1       13.4      25.6    2590.
  1   12 : 28 : 30     0.065     0.0      0.006       0.7       0.6       13.2      25.8    2600.
  1   12 : 28 : 45     0.066     0.0      0.0         0.9       0.6       13.3      25.6    2560.
  1   12 : 29 :  0     0.068     0.0      0.006       0.8       1.1       13.5      25.7    2600.
  1   12 : 29 : 15     0.065     0.0      0.008       0.8       0.7       13.4      25.7    2580.
  1   12 : 29 : 30     0.068     0.0      0.013       0.8       0.9       13.4      25.5    2580.
  1   12 : 29 : 45     0.075     0.0      0.011       0.7       1.0       13.6      25.7    2550.
  1   12 : 30 :  0     0.072     0.002    0.007       0.8       0.7       13.7      25.6    2560.
  1   12 : 30 : 15     0.074     0.0      0.0         0.7       0.5       13.8      25.5    2580.
  1   12 : 30 : 30     0.072     0.0      0.0         0.8       1.2       13.7      25.7    2560.
  1   12 : 30 : 45     0.072     0.0      0.0         0.8       0.5       13.6      25.6    2560.
```

SECTION 5.0

QUALITY CONTROL AND QUALITY ASSURANCE PROGRAMS

5.1 INTRODUCTION

The RTI quality control program for the Tulsa study began with preliminary tests of analyzer performance and a training program for field personnel prior to field monitoring. Also, the traceability of calibration gases to NBS Standard Reference Material was established. Once in Tulsa, a program consisting of monthly (or more frequent) multipoint dynamic calibrations of each continuous analyzer, daily zero and span response checks, and standard stripchart data reduction procedures was established.

EPA was responsible for maintaining a quality assurance program for the eight-station RTI monitoring network as well as for the two ozone monitoring stations maintained by the Tulsa City/County Health Department. PEDCo Environmental (under contract to EPA, Environmental Monitoring Support Laboratory), and the EPA Region VI Quality Assurance Office (Dallas, Texas) each conducted a series of quantitative onsite performance audits to collect information on the accuracy of the continuous pollutant measurements for ozone, nitric oxide, and nitrogen dioxide. Other quality assurance measures included "blind" audits of the Beckman 6800 air quality chromatographs using EPA-verified methane in air mixtures and quality control activities associated with the sampling and analysis of individual hydrocarbon species. Much of the data derived from quality control/quality assurance efforts have been tabulated and statistically examined.

Quality control and quality assurance aspects of the airborne air quality measurements portion of this project are included in Section 4.0 of this volume. Quality control aspects of the Tenax GC/MS/COMP studies are discussed in Appendix B of this volume.

5.2 QUALITY CONTROL AND QUALITY ASSURANCE AT SURFACE SITES

5.2.1 Preliminary Testing

Prior to leaving Research Triangle Park for Tulsa, RTI operated and calibrated each government-furnished ambient air analyzer. Also prior to departure, three RTI project members were verified at the EPA Quality Assurance Branch Laboratory in the conduct of the gas phase titration method[3] of NO by O_3 as a means for calibrating ozone and oxides of nitrogen analyzers. One of these three persons was assigned the responsibility for monthly multipoint calibrations of all ambient analyzers. The results of these calibration verifications are given in Table 5.1. Proper operation of two different calibration systems was also verified at the EMSL QAB Laboratory. The concentrations of ten different NO in nitrogen calibration standards (in aluminum cylinders) were also verified at EPA's QAB Laboratory by comparison to NBS standard reference material prior to (and following) the field study. The results of the calibration standards verification and referencing are shown in Table 5.2.

Table 5.1. Comparison of RTI GPT Calibration Concentrations to EPA Quality Assurance Branch

	Concentration, ppm					
Gas	QAB	RTI[a]	QAB	RTI[b]	QAB	RTI[c]
NO	0.001	0.000	0.000	0.000	0.000	0.000
	0.102	0.110	0.394	0.397	0.402	0.405
	0.192	0.205			0.298	0.304
	0.277	0.288			0.198	0.203
	0.373	0.385				
NO_2	-0.002	0.000	0.007	0.000	0.000	0.000
	0.082	0.082	0.097	0.094	0.345	0.345
	0.164	0.163	0.187	0.186	0.173	0.170
	0.252	0.252	0.217	0.214		
			0.278	0.279		
O_3	0.000	0.000	0.000	0.000	0.000	0.000
	0.084	0.082	0.092	0.095	0.341	0.346
	0.166	0.163	0.184	0.188	0.176	0.166
	0.255	0.252	0.217	0.216		
			0.282	0.281		

[a] Operator #1; [b] Operator #2; [c] Operator #3.

Table 5.2. NO in N_2 Calibration Standards Used in Tulsa. Results of EPA Quality Assurance Branch Analyses

Cylinder Number	Location	[NO], ppm June 1977[a]	[NO], ppm December 1977
LL 3393	Skiatook Lake	51.5	49.9
LL 3398	Sperry (until 9/20/77)	51.5	49.9
LL 3401	Sperry (after 9/20/77)	51.6	50.1
LL 3402	Spare	51.6	50.1
LL 3416	Post Office	51.3	49.8
LL 3418	Public Health Department	51.3	50.1
LL 3422	Ochelata	51.3	49.9
LL 3423	Vera	51.3	49.9
LL 3425	Wynona	51.5	50.0
LL 3429	Liberty Mounds	51.2	50.0

[a] These were the values used to generate calibration standards in the field.

Field personnel were familiarized with EPA procedures for visually reducing strip chart data and reporting hourly data in SAROAD format. Supervised training in instrument operation, monitoring techniques, and data reduction qualified the field personnel for the study.

5.2.2 Methods of Quality Control in Tulsa

To maintain a high level of confidence in the air quality data, RTI routinely monitored critical instrument parameters. Daily checksheet entries indicated consistency or variability of instrument parameters such as flow rate, pressure, and temperature. Daily zeros and spans were performed on the ozone and NO/NO_2 analyzers. Zero and span gases for the ozone analyzer were provided from the instrument's internal scrubber and ultraviolet lamp. Zero and span gases for the NO/NO_2 analyzers were provided from an external calibrator by dilution of certified NO in N_2 mixtures and by gas phase titration of NO by ozone. Zero and span results served as indicators of instrument drift. When zero drift exceeded 0.01 ppm (±2 percent of 0.5 ppm full scale) during a 24-hr period, the data of the preceding 24-hr period were critically examined and questionable hours were invalidated. If a span drift of ±15 percent of full scale (0.5 ppm) occurred, the instrument was immediately recalibrated or replaced and the data recorded during the period of span drift were invalidated.

Monthly multipoint dynamic calibrations by gas phase titration were carried out for each ozone and oxide of nitrogen analyzer in the monitoring network.[3] The same person performed every calibration using a single EPA-verified calibration apparatus and verified NO in N_2 calibration cylinders that were kept at each station.

Estimates of measurement precision of the continuous ozone analyzers were derived from a comparison of precalibration span concentration (as calculated from the calibration curve of the preceding calibration) with the predicted span concentration based on gas phase titration. To determine these estimates, the means, standard deviations, and coefficients of variation were derived for each of the series of precalibration span points. The coefficients of variation were used to establish confidence intervals within 90 percent probability limits. The 90 percent probability limits were calculated using the following equations:[9]

$$\text{Upper 90 percent probability limit} = A_L + 1.64\ (S_{pi})$$

$$\text{Lower 90 percent probability limit} = A_L - 1.64\ (S_{pi})$$

where:

A_L = the mean of the percent differences between observed and expected span values.

S_{pi} = the standard deviation about the mean of the percent differences between observed and expected values.

The interpretation of this estimate of precision is that one would expect 90 percent of the individual span measurements to fall within the calculated confidence intervals for the period of measurement encompassed by the calibration and precalibration dates. Comparison of predicted and observed ozone span concentrations at the time of precalibration is given in Table 5.3. Precision estimates for each of the continuous ozone analyzers are given in Table 5.4.

Table 5.3. Comparison of predicted and observed ozone values at the time of analyzer "precalibration." Tulsa, Oklahoma monitoring stations, summer, 1977

	Date		Concentration, ppm		
Station	Calibration	Pre-Calibration	Observed	Predicted	% Difference
Liberty Mounds	6/28	7/02	0.214	0.210	+ 1.9
	7/02	7/30	0.295	0.297	- 0.7
	7/30	9/01	0.132	0.158	-16.5
	9/01	9/28	0.134	0.135	- 0.7
Tulsa Post Office	7/16	8/05	0.136	0.135	+ 0.7
	8/05	8/28	0.135	0.121	+11.6
	8/28	9/26	0.132	0.130	+ 1.5
Tulsa City/ County Health Department	7/07	8/06	0.141	0.124	+13.7
	8/06	8/22	0.192	0.168	+14.3
	8/22	8/27	0.136	0.132	+ 3.0
	8/27	9/25	0.210	0.212	- 0.9
Sperry	8/02	8/25	0.192	0.196	- 2.0
	8/25	9/14	0.293	0.242	+21.1
	9/14	9/18	0.145	0.145	0
	9/18	9/26	0.179	0.181	- 1.1
Skiatook Lake	8/09	8/29	0.132	0.120	+10.0
	8/29	9/29	0.130	0.129	+ 0.8
Wynona	7/20	8/04	0.143	0.164	-13.0
	8/04	8/28	0.133	0.140	- 5.0
	8/28	9/26	0.131	0.135	- 2.9
Vera	6/30	7/05	0.105	0.096	+ 9.4
	7/05	7/29	0.124	0.113	+ 9.7
	7/29	9/09	0.132	0.121	+ 9.7
	9/09	9/26	0.134	0.133	+ 0.8
Ochelata	6/29	8/07	0.137	0.136	+ 0.7
	8/07	8/30	0.135	0.130	+ 3.8
	8/30	9/26	0.135	0.132	+ 2.2

Table 5.4. Estimates of precision of measurements based on precalibration span values for ozone analyzers in Tulsa, Oklahoma

Station	Mean Difference (%)	Upper Range Limit (%)	Lower Range Limit (%)
Liberty Mounds	-4.0	+9.8	-17.8
Tulsa Post Office	+4.6	+11.5	-8.5
Health Department	+7.5	+14.4	-10.6
Sperry	+4.5	+19.3	-17.1
Skiatook Lake	+5.4	+13.4	-7.9
Wynona	-7.0	+6.4	-11.0
Vera	+7.4	+3.4	-7.2
Ochelata	+0.8	+5.2	-4.6

It should be emphasized that the estimates of precision given in Table 5.4 are based on some precalibration spans performed a day or two after a zero or span drift was noted. The instrument was calibrated to correct the problem and the data from the point of the zero or span drift was invalidated or corrected based on the new calibration. Thus the reader should not infer that data from the entire period of analyzer performance prior to the precalibration check was out of agreement by the percentage stated. The percentages given in Table 5.4 thus represent the "worst case" based on available data and should be compared to the results of the performance audits given in Section 5.2.4.

Another quality control measure was extensive data validation. All hourly data were checked against analyzer performance prior to reporting the data. Occurrences of unusual measurement trends, power failures, and strip chart problems were noted for use in future data validation. The data were initially checked by RTI. Next the SAROAD hourly data forms and the computer printout derived from them were validated at EPA using specifications established by the EPA Environmental Monitoring Support Laboratory.

5.2.3 Quality Assurance Qualitative Systems Audit

The objective of the onsite qualitative systems audit (performed by a representative of the EPA Office of Air Quality Planning and Standards) was to assess the potential of the operator and calibration systems to generate data of acceptable quality for the duration of the summer study. In concurrence with the first quantitative audit, an onsite qualitative systems audit was performed. This audit included a verification of the procedures used in calibration through a review of written procedures and observation of a calibration, and an inspection of the station, including sampling probe, manifold, and instrumentation. Results of this qualitative audit were favorable.

5.2.4 Quality Assurance Performance Audits

The objective of the onsite performance audits was to collect information on the accuracy of the summer study ozone, oxides of nitrogen, and meteorological measurements. During the summer study, audit teams from PEDCo Environmental and EPA Region VI visited each Tulsa monitoring station on three occasions for a total of six audits.

The procedure used by PEDCo to audit the continuous analyzers at each station consisted of challenging the respective analyzers with known concentrations of pollutants at three points. Test concentrations of nitric oxide were generated by diluting (with zero air) a 43.7 ppm NBS-SRM NO standard cylinder. Nitrogen dioxide concentrations were generated by gas phase titration of the NO standard with ozone to produce NO_2. Test concentrations of ozone were generated using an ultraviolet ozone generator calibrated by gas phase titration of NO.

The generated concentrations were introduced to the analyzers through a glass manifold to which the instrument's sample inlet was attached. Analyzer response was determined by reduction of the signal from the strip chart record and application of the appropriate transfer equation, which converted percent of chart to ppm and had been calculated at the time of the preceding multipoint calibration. Results of the PEDCo quantitative audits for ozone and oxides of nitrogen analyzers are given in Table 5.5.

Table 5.5. Summary of PEDCo Environmental Audit Results

Audit Date	NO			NO_2			O_3		
	Audit	Analyzer	% Difference	Audit	Analyzer	% Difference	Audit	Analyzer	% Difference
					Liberty Mounds				
July 13	0.0	-0.01	--	0.0	0.0	--	0.0	0.0	--
	0.172	0.185	+7.6	0.178	0.180	+1.1	0.178	0.158	-11.2
	0.343	0.379	+10.5	0.386	0.390	+1.0	0.386	0.337	-12.7
August 8	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.150	0.168	+12.0	0.203	0.208	+2.5	0.203	0.210	+3.4
	0.320	0.361	+12.8	0.399	0.407	+2.0	0.399	0.404	+1.3
September 7	0.0	0.0	--	0.0	0.012	--	0.0	0.0	--
	0.179	0.186	+4.0	0.163	0.167	+2.5	0.163	0.156	-4.3
	0.321	0.335	+4.4	0.375	0.367	-2.1	0.375	0.358	-4.5
					Health Department				
July 11	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.073	0.076	+4.1	0.110	0.112	+1.8	0.110	0.097	-11.8
	0.184	0.183	-0.5	0.210	0.211	+0.5	0.210	0.195	-7.1
	0.389	0.399	+2.6	0.365	0.362	-0.8	0.365	0.357	-2.2
August 12	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.158	0.159	+0.6	0.199	0.200	+0.5	0.199	0.206	+3.5
	0.335	0.348	+3.9	0.388	0.374	-3.6	0.388	0.405	+4.4
September 10	0.0	0.002	--	0.0	0.0	--	0.0	0.0	--
	0.136	0.145	+6.6	0.195	0.195	0.0	0.195	0.189	-3.1
	0.314	0.337	+7.3	0.401	0.395	-1.5	0.401	0.392	-2.0

(continued)

Table 5.5. (continued)

Audit Date	NO			NO_2			O_3		
	Audit	Analyzer	% Difference	Audit	Analyzer	% Difference	Audit	Analyzer	% Difference
				Post Office					
July 12	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.147	0.139	-5.4	0.148	0.148	0.0	0.148	0.155	+4.7
	0.367	0.361	-1.6	0.394	0.402	+2.0	0.394	0.412	+4.6
August 10	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.175	0.171	-2.3	0.178	0.172	-3.4	0.178	0.186	+6.2
	0.384	0.364	-5.2	0.373	0.364	-2.4	0.373	0.396	+4.5
September 11	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.129	0.125	-3.1	0.181	0.184	+1.6	0.181	0.180	-0.6
	0.323	0.325	+0.6	0.371	0.372	+0.5	0.371	0.370	-0.3
				Sperry					
July 13	0.0	0.006	--	0.0	-0.001	--	0.0	0.006	--
	0.132	0.134	+1.5	0.189	0.185	-2.1	0.189	0.201	+6.3
	0.395	0.394	-0.3	0.375	0.370	-1.3	0.375	0.386	+2.9
August 11	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.174	0.178	+2.3	0.207	0.209	+1.0	0.207	0.216	+4.4
	0.363	0.365	+0.6	0.376	0.383	+1.9	0.376	0.394	+4.8
September 9	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.416	0.385	-7.5	0.152	0.154	+1.3	0.152	0.154	+0.3
	0.148	0.135	-8.9	0.313	0.318	+1.7	0.313	0.314	+1.5

Table 5.5. (continued)

Audit Date	NO Audit	NO Analyzer	NO % Difference	NO_2 Audit	NO_2 Analyzer	NO_2 % Difference	O_3 Audit	O_3 Analyzer	O_3 % Difference
					Vera				
July 14	0.0	0.0	--	0.0	0.0	--	0.0	-0.009	--
	0.166	0.178	+7.2	0.205	0.219	+6.8	0.205	0.207	+1.0
	0.339	0.371	+9.4	0.407	0.435	+6.9	0.407	0.416	+2.2
August 10	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.176	0.172	-2.1	0.181	0.178	-1.7	0.181	0.185	+2.2
	0.364	0.375	+3.1	0.351	0.348	-0.9	0.351	0.360	+2.6
September 8	0.0	0.007	--	0.0	0.0	--	0.0	0.001	--
	0.195	0.188	-3.6	0.179	0.176	-1.8	0.179	0.169	-5.6
	0.346	0.352	+1.7	0.362	0.359	-0.8	0.362	0.341	-5.8
					Skiatook Lake				
July 14	0.0	0.0	--	0.0	0.0	--	0.0	-0.007	--
	0.168	0.163	-3.0	0.166	0.163	-1.8	0.166	0.161	-3.0
	0.388	0.367	-5.4	0.337	0.340	+0.9	0.337	0.343	+1.8
August 11	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.155	0.153	-1.3	0.190	0.190	0.0	0.190	0.181	-3.5
	0.351	0.355	+1.1	0.368	0.371	+0.8	0.368	0.355	-4.7
September 8	0.0	0.0	--	0.0	-0.005	--	0.0	0.0	--
	0.198	0.194	-2.0	0.175	0.174	-0.6	0.175	0.186	+6.3
	0.392	0.361	-7.9	0.347	0.361	+4.0	0.347	0.370	+6.6

Table 5.5. (continued)

Audit Date	NO			NO_2			O_3		
	Audit	Analyzer	% Difference	Audit	Analyzer	% Difference	Audit	Analyzer	% Difference
					Wynona				
July 15	0.0	0.0	--	0.0	0.0	--	0.0	-0.008	--
	0.155	0.175	+12.9	0.195	0.210	+7.8	0.195	0.184	-5.6
	0.326	0.367	+12.6	0.358	0.390	+8.9	0.358	0.346	-3.4
August 10	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.148	0.170	+15.1	0.145	0.184	+27.3	0.145	0.161	+11.3
	0.328	0.376	+14.6	0.322	0.361	+12.3	0.322	0.321	-0.2
September 8	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.146	0.162	+11.0	0.194	0.211	+8.9	0.194	0.189	-2.6
	0.331	0.367	+10.9	0.342	0.368	+7.7	0.342	0.333	-2.6
					Ochelata				
July 15	0.0	0.004	--	0.0	0.0	--	0.0	0.0	--
	0.178	0.192	+7.9	0.197	0.201	+2.0	0.197	0.185	-6.1
	0.323	0.347	+7.4	0.383	0.396	+3.4	0.383	0.368	-3.9
August 9	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.153	0.169	+10.4	0.185	0.181	-2.2	0.185	0.170	-8.1
	0.329	0.362	+10.2	0.379	0.380	+0.3	0.379	0.351	-7.4
September 10	0.0	0.0	--	0.0	0.0	--	0.0	0.0	--
	0.176	0.163	-7.4	0.180	0.184	+2.3	0.180	0.202	+12.0
	0.356	0.341	-4.2	0.365	0.378	+3.5	0.365	0.411	+12.7

Table 5.6. Percent error for ozone

Location	$\bar{x}$[a]	S_d[b]	Percent error at 90% confidence level[c]
Liberty Mounds	-4.7	±6.45	$-15.3 \leq \%E \leq 5.9$
Tulsa Health Department	-2.9	±5.50	$-11.9 \leq \%E \leq 6.1$
Post Office	+3.2	±2.88	$-1.5 \leq \%E \leq 7.9$
Sperry	+3.4	±2.23	$-0.2 \leq \%E \leq 7.1$
Vera	-0.57	±4.01	$-7.2 \leq \%E \leq 6.0$
Skiatook Lake	+0.58	±5.06	$-7.7 \leq \%E \leq 8.9$
Wynona	-0.52	±6.04	$-10.5 \leq \%E \leq 9.4$
Ochelata	-0.13	±9.78	$-16.2 \leq \%E \leq 16.0$

[a] $\bar{x}$ is average of the $\bar{x}$'s for the three separate PEDCo audits.

[b] S_d = standard deviation about the mean of the percent differences between observed and expected values.

[c] Upper limit = $\bar{x} + 1.64\ (S_d)$. Lower limit = $\bar{x} - 1.64\ (S_d)$.

Confidence intervals or "error bands" were derived from the ozone audit results. Table 5.6 lists the percent error for the 3-month period for each monitoring station. This is representative of that ozone analyzer's accuracy for the period. The overall ozone network "error band" (i.e., for the eight-station network) is:

$$-7.3 \leq \%E \leq +5.7.$$

5.2.5 Audit of Continuous Hydrocarbon Monitors

Ambient air chromatographs were operated at three sites in Tulsa during the summer of 1977. "Blind" samples of methane in air mixtures were supplied to the contractor by EPA's Quality Assurance Branch Laboratory. The results of the use of these audit mixtures are given in Table 5.7. The agreement is excellent.

Table 5.7. Audit results of methane in air standards, ppm, Tulsa, 1977

Location/date	Audit concentration	Analyzer response	Percent difference
Tulsa Health Department	2.06	2.05	-0.5
8/6/77	2.96	2.98	+0.7
	4.40	4.49	+2.0
Post Office	2.06	2.03	-1.5
8/9/77	2.96	2.96	0.0
	4.40	4.43	+0.7
Wynona	2.06	2.04	-1.0
9/11/77	2.96	2.96	0.0
	4.40	4.35	-1.1

5.3 QUALITY CONTROL PROCEDURES ASSOCIATED WITH HYDROCARBON ANALYSES BY GC-FID

5.3.1 Introduction

An extensive quality control program for sampling and analysis of individual hydrocarbons was followed during this study. Before any ambient air field samples were taken, the stainless steel sampling containers were evaluated for cleanliness, storage characteristics, and the best methods for collection and withdrawal of sample. During the field study, monthly quantitative calibrations of the chromatographic columns were performed. The program of the computerized data acquisition system was updated based on the retention times, which were checked twice weekly. For details of sampling and analytical methodology, refer to Appendix A of this volume.

A further quality control measure was the visual examination of every chromatogram and the assignment of peak identifications using relative retention times and pattern recognition techniques. This step was necessary since limitations of the data acquisition system prevented its correctly identifying all peaks or assigning an area count to peaks having poor slope characteristics.

Finally, experiments were conducted to examine the extent of "decay" of hydrocarbon compounds held in stainless steel containers for up to 30 days. Both laboratory-prepared mixtures and ambient air samples were tested.

5.3.2 Sample Container Evaluation

Evaluations of hydrocarbon sample containers by RTI in past studies have pointed to the stainless steel container as a good choice for the purpose of collecting ambient air samples. Such containers were used exclusively in both the ground and aircraft monitoring programs in Tulsa.

Controlled experiments were conducted to evaluate the stainless steel container and the stability of the various hydrocarbons at concentrations similar to those found in ambient air. The effects of NO, NO_2, and O_3 on the components of each mixture were also sought.

One of the hydrocarbon mixtures employed in the test was composed of ethane, ethylene, acetylene, propane, propylene, and n-pentane. Each test was conducted over an 18-day period with more intensive analyses during the earlier part of the test. Samples were withdrawn from the containers on days 0, 1, 2, 3, 4, 8, 13, and 18. From day 1 to day 4, samples were analyzed on a random basis to minimize any systematic error in the analyses.

Figures 5.1 through 5.4 show the results of the evaluation of C_2-C_5 compounds by plotting the ppb (V/V) concentration of the individual hydrocarbon compounds versus the day of analysis. It should be noted that the pumping system employed to pressurize the container during field collection in Tulsa has been shown to destroy ozone at concentrations of 0.3 ppm.

In these experiments, the stainless steel containers were not heated during the time of sample withdrawal. It was found that heating the container to a temperature of 70° C gave a more quantitative transfer of hydrocarbons and did not alter the sample. For this reason, the sampling cylinders were heated in all analyses for the Tulsa field study.

5.3.3 Zero Air Evaluation

The zero air experiment provided data on the potential for contamination of the sample while stored or shipped in the container. The zero air had been previously analyzed for trace hydrocarbons and was found to contain only trace quantities (~20 ppb [V/V]) of ethylene. It was later discovered that the ethylene was eluting from a small piece of Teflon tubing (FEP) between the sampling containers and the zero air source. This problem was solved by replacing the Teflon tubing with flexible stainless steel tubing. The zero air was introduced to the inside of the containers after it had

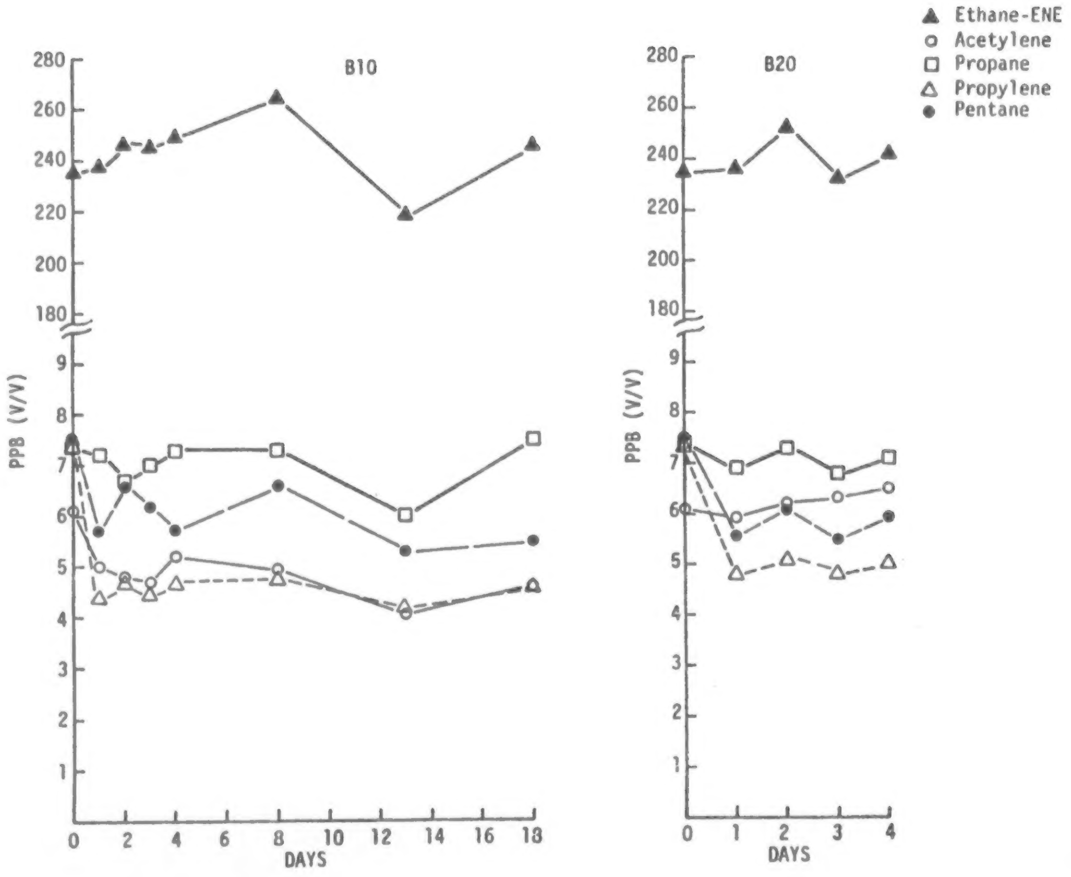

Figure 5.1. Stainless steel container evaluation (HC's and zero air).

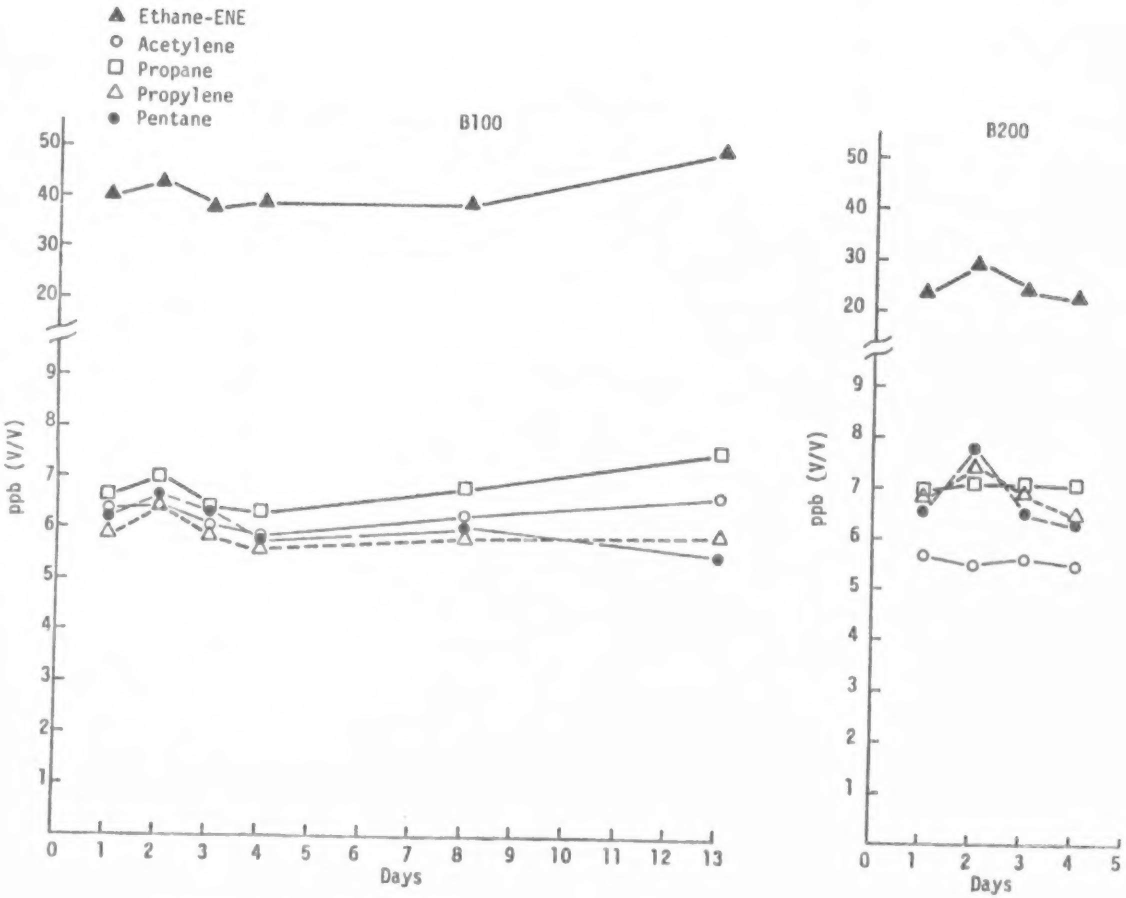

Figure 5.2. Stainless steel container evaluation (HC's, zero air, and 0.01 ppm NO).

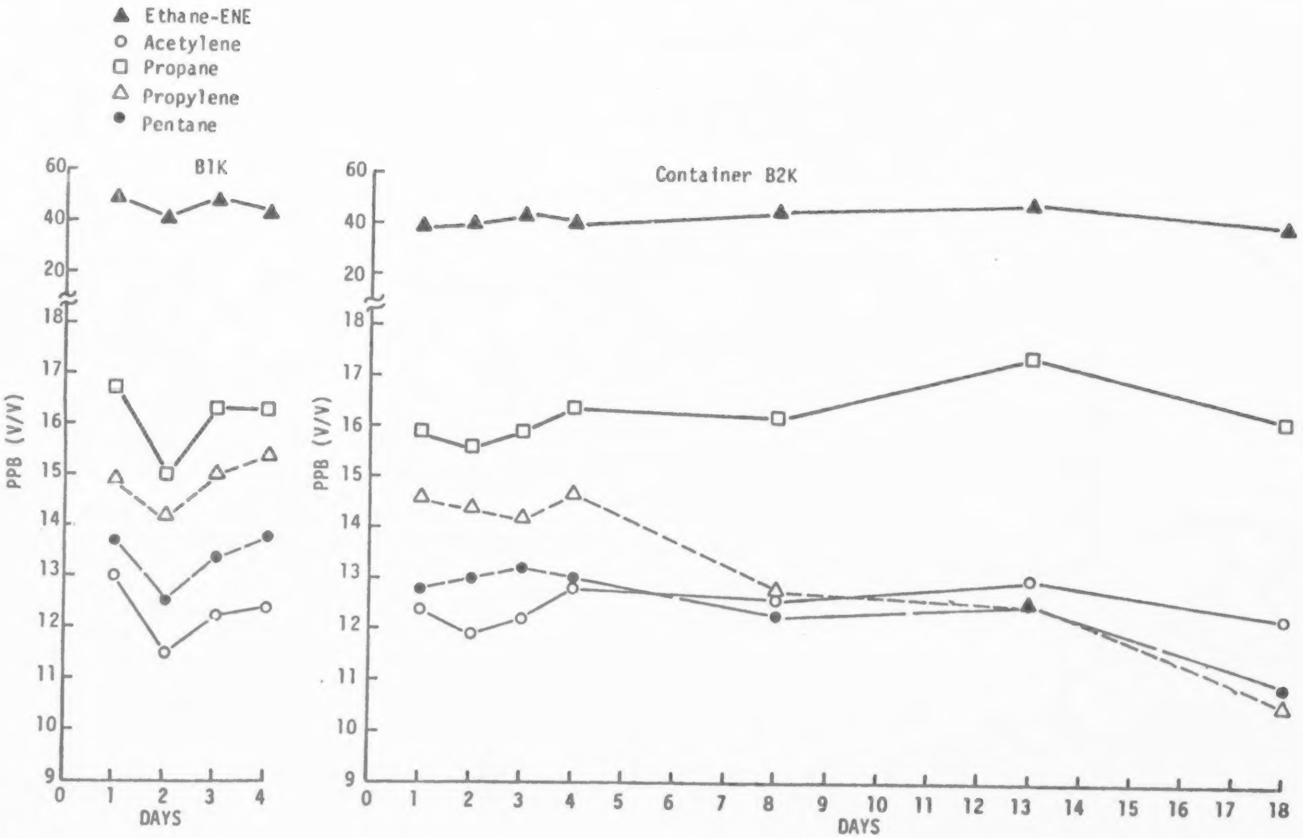

Figure 5.3. Stainless steel container evaluation (HC's, zero air, and 0.01 ppm NO_2).

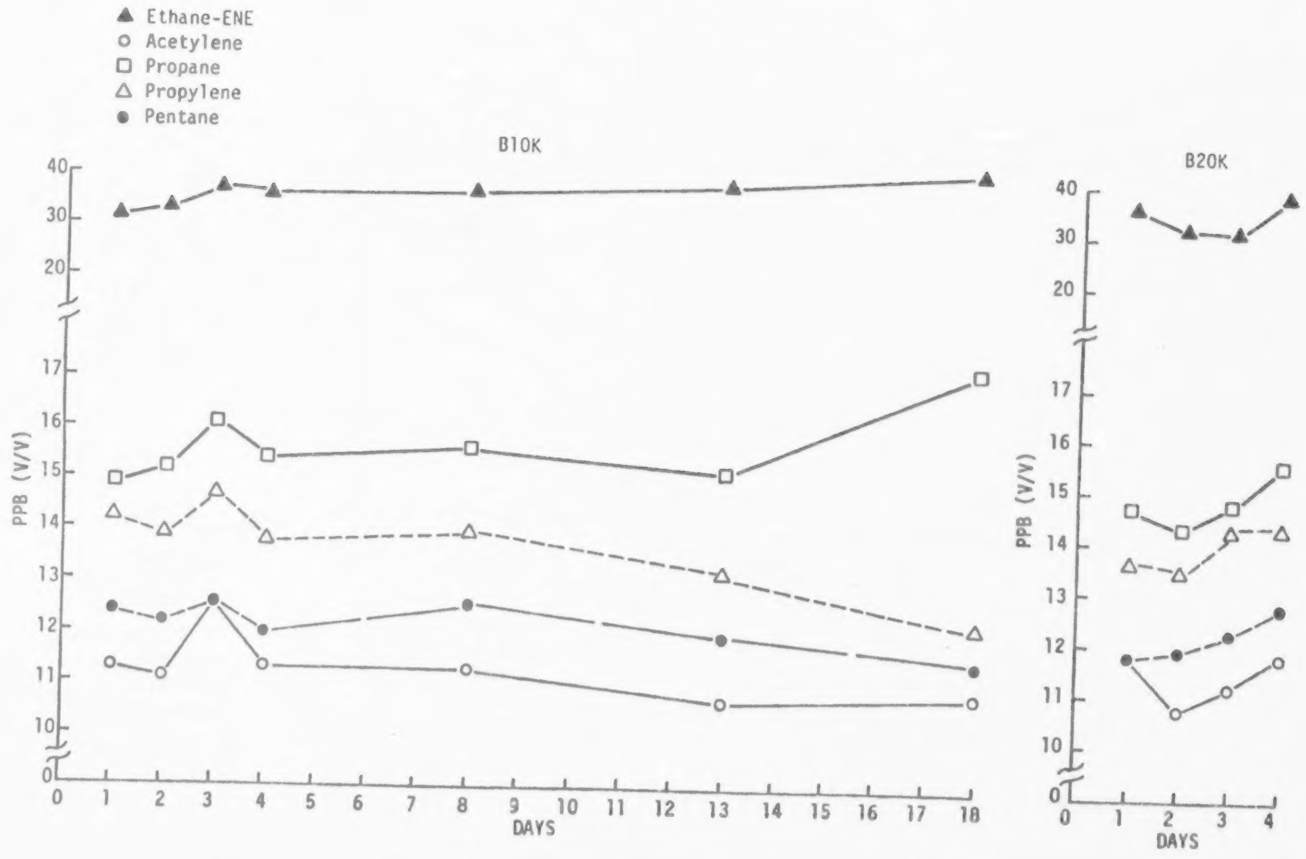

Figure 5.4. Stainless steel container evaluation (HC's, zero air, and 0.1 ppm O_3).

passed through a double dilution system that was later employed to generate low concentrations of hydrocarbons and other pollutants.

The zero air test samples in the containers were analyzed for both C_2-C_5 and C_5-C_{10} hydrocarbons over a period of days. The stainless steel container showed a slight decrease in the ethylene concentration from 20 ppb to 12 ppb (18th day). After 18 days, no other components were detected in the analyses. It should be pointed out that the stainless steel containers had been pressurized to 40 psig with the use of an MB 151 metal bellows pump. The absence of contamination over such an extended period is important. Since in many cases, sampling containers are transported in contaminated atmospheres, it is imperative that the samples retain their integrity even though the containers are exposed to pollutant levels several orders of magnitude higher than those of the collected sample.

In another test, containers were filled with zero air, shipped by air freight to the study area and sent back to RTI for analysis. QC samples 3 and 4 were shipped on July 19, 1977, and returned on July 28, 1977. QC samples 5 and 6 were shipped on August 3, 1977, and returned to RTI on August 12, 1977. Results of these analyses are given in Table 5.8. From these samples it was concluded that the sample integrity had not been altered during the transit period, and no material outgassed from the inside surface of the container.

5.3.4 Hydrocarbon Mixture Quality Control Samples

From the beginning of RTI's experience with captive air samples, concern has been focused on the stability of these samples in various containers. Detailed discussions of the RTI efforts in the field of container evaluation can be found elsewhere.[5] [10] As a result of several studies, the stainless steel bottle, closed with a stainless steel bellows valve, has proved to be the most practical container for general ambient hydrocarbon sampling.

Two major factors affecting sample stability are (1) adsorption of the hydrocarbon species onto the walls of the container, and (2) chemical breakdown of hydrocarbons from reactions with oxygen, ozone, NO_x, etc., in the ambient sample. These factors were evaluated in an in-house program that has become known as the "Wade Avenue Study."

Table 5.8. Results of the Analyses of Zero Air Stored in Stainless Steel Containers

Sample #	QC 3	QC 4	QC 5	QC 6
Analysis Date	7/28/77	7/28/77	8/12/77	8/12/77
Methane				
Ethane	ppbC	ppbC	ppbC	ppbC
Ethylene	—	—	—	—
Propane	2.0	1.7	3.0	1.6
Acetylene	—	—	—	—
Isobutane	—	—	—	—
n-Butane	—	—	—	—
Propylene	—	—	—	—
Isopentane	0.2	—	1.3	—
n-Pentane	—	—	—	—
Cyclopentane	—	—	—	—
Isoprene	—	—	—	—
2-2 Dimethylbutane	—	—	0.4	0.5
2-Methyl pentane	—	—	—	—
3-Methyl pentane	—	—	0.5	—
1-Hexene	—	—	—	—
2-Methyl pentene-1	—	—	0.5	—
n-Hexane	—	—	—	—
2-4 Dimethylpentane	—	—	—	—
Cyclohexane	2.7	4.0	—	—
3-Methylhexane	—	—	—	2.0
2,2,4 Trimethylpentane	—	—	—	—
n-Heptane	2.3	—	0.2	—
Methyl cyclohexane	—	—	—	—
2,3,4 Trimethylpentane	—	—	—	—
3-Methylheptane + Isooctane	—	—	—	—
n-Octane	—	—	—	—
n-Nonane	—	—	0.1	—
n-Decane	—	—	0.1	—
n-Undecane	—	—	—	—
n-Dodecane	—	—	—	—
Benzene	—	—	—	—
Toluene	1.1	0.4	0.5	0.6
Ethyl benzene	—	—	—	—
p-xylene	—	—	—	—
m-xylene	—	—	—	—
o-xylene	—	—	—	—
n-Propyl benzene	—	—	—	—
1,3,5-Trimethylbenzene	—	—	—	—
m-Ethyl toluene	—	—	—	—
t-Butyl benzene	—	—	—	—
o-Ethyl toluene	—	—	—	—
α pinene + β pinene	—	—	—	—
1,2,4-Trimethylbenzene	—	—	—	—
1,2,3-Trimethylbenzene	—	—	—	—
n-Butyl benzene	—	—	—	—
	—	—	—	—

A complex mixture of C_5-C_{10} aliphatic hydrocarbons was diluted to a concentration of ~20 ppb V/V per component in dry, hydrocarbon-free air. Four stainless steel containers were filled with this mixture and analyzed over a 30-day period. The results of these analyses can be found in Tables 5.9-5.13.

The greatest concentration variability is shown in three compounds: isoprene, cyclohexane, and 2-methyl-1-pentene. The cyclohexane numbers are somewhat in question, however. If any water is present in a sample, it forms a false peak on the OV-101 column which, in this analysis program, corresponds to the cyclohexane elution time. This peak is not very reproducible. Therefore, the cyclohexane concentration fluctuations may be due to traces of water vapor that passed through the column.

Isoprene (2-methyl-1,3-butadiene) and 2-methyl-1-pentene share a common trait, a methyl-substituted double bond. Because of their structure, these compounds might be expected to be more reactive than are the straight-chain single or double bonds, or the methyl-substituted single bonds.

The heaviest straight-chain hydrocarbon, decane, showed a gradual decay trend. This could probably be attributed to adsorption on the container wall since this compound would not be expected to be very reactive.

To evaluate the effects of oxidants, moisture, and other components of typical urban ambient air, three samples were taken by split sampling technique on the roadside of Wade Avenue, Raleigh, N.C., at the early morning rush hour. The samples were analyzed for C_2-C_5 light hydrocarbons, C_5-C_{10} aliphatics, and C_6-C_{10} aromatics. The samples were analyzed over a 19-day period and the results are shown in Tables 5.14-5.16. On the whole, these analyses showed more variability than did the laboratory mixes. The compounds with unsaturated bonds and those with methyl substitutents showed the greatest changes in concentration. Also, the heaviest aliphatic and aromatic compounds showed a decreasing concentration trend. On the whole, however, the concentrations of most components remained quite stable over the 19-day period.

5.3.5 Calibration Procedures

Periodic calibration was carried out to insure accuracy in both the quantitative and qualitative aspects of the analyses. The aliphatic and aromatic standard mixtures were prepared at RTI by injecting appropriate

Table 5.9: Laboratory Decay Study of C_5-C_{10} Hydrocarbons; Concentrations in ppbV

Sample Number A-6	Day of Analysis										Mean	Standard Deviation
	1	5	6	9	12	16	19	23	26	30		
Isoprene	37.9		40.2		37.0		37.8	31.8	34.9	32.4	36.0	3.1
2,2-Dimethylbutane	23.4		25.6		25.4		25.0	22.0	22.9	24.0	24.0	1.4
2-Methylpentane	30.4		29.6		30.5		30.7	28.9	30.6	29.4	30.0	0.7
3-Methylpentane	40.0		40.9		43.3		41.1	39.2	41.0	42.7	41.2	1.4
1-Hexene	47.7		47.0		48.3		48.1	46.7	48.6	47.3	47.7	0.7
2-Methylpentene	84.8		84.8		88.2		85.1	84.1	86.7	85.0	85.5	1.4
2,4-Dimethylpentane	26.7		24.3		24.5		25.7	26.7	27.7	27.8	26.2	1.4
Cyclohexane	65.2		73.5		65.7		60.4	68.9	71.7	70.3	68.0	4.5
3-Methylhexane	41.9		40.2		39.5		42.2	42.6	44.4	44.4	42.2	1.9
2,2,4-Trimethylpentane	54.6		53.5		54.4		56.4	56.9	58.4	58.8	56.1	2.1
n-Heptane	36.0		35.3		35.5		36.9	36.7	37.2	37.9	36.5	0.9
Methylcyclohexane	28.8		28.7		28.8		29.6	29.1	29.6	30.0	29.2	0.5
2,3,4-Trimethylpentane	26.5		26.8		26.9		26.7	25.9	26.1	26.3	26.5	0.4
3-Methylheptane	25.0		27.0		27.1		26.5	25.1	24.9	25.6	25.9	1.0
n-Octane	26.2		26.7		26.9		26.3	25.7	25.4	26.0	26.2	0.5
n-Nonane	20.7		25.3		25.6		24.2	23.3	22.8	23.5	23.6	1.6
n-Decane	18.1		17.1		15.1		14.9	14.9	15.5	14.5	15.7	1.3

Table 5.10. Laboratory Decay Study of C_5-C_{10} Hydrocarbons; Concentrations in ppbV

Sample Number A-30	Day of Analysis										Mean	Standard Deviation
	1	5	6	9	12	16	19	23	26	30		
Isoprene	33.4	45.3	43.8	37.6	39.2	42.8	38.0	32.7	30.7	27.9	37.1	5.9
2,2-Dimethylbutane	24.4	27.5	27.6	28.0	27.8	27.4	29.2	25.9	24.8	25.7	26.8	1.5
2-Methylpentane	30.1	32.5	34.0	31.6	33.1	33.6	33.9	33.1	34.0	32.4	32.8	1.2
3-Methylpentane	37.3	40.9	41.3	42.5	42.8	42.1	42.3	40.8	40.8	42.7	41.3	1.6
1-Hexene	45.0	47.8	49.3	47.5	48.0	48.1	49.4	52.3	48.7	46.4	48.2	1.9
2-Methylpentene	104.1	106.5	105.9	109.1	111.9	106.1	107.8	103.3	99.3	97.4	105.1	4.3
2,4-Dimethylpentane	30.1	30.6	31.1	31.0	30.9	30.6	31.2	31.0	30.0	30.2	30.7	0.4
Cyclohexane	61.6	64.0	59.1	59.5	52.0	62.5	58.9	46.8	49.8	47.9	56.2	6.4
3-Methylhexane	39.6	39.7	37.8	37.9	36.5	36.9	37.8	36.4	36.9	37.5	37.7	1.2
2,2,4-Trimethylpentane	63.3	63.8	62.6	63.3	63.6	62.3	64.4	65.1	62.5	63.8	63.5	0.9
n-Heptane	37.3	36.5	35.1	35.5	35.5	34.5	36.2	35.0	34.5	34.5	35.5	0.9
Methylcyclohexane	35.4	34.2	33.7	33.8	34.3	33.2	34.7	33.6	33.3	33.6	34.0	0.7
2,3,4-Trimethylpentane	28.1	29.6	30.1	30.2	30.0	29.7	30.1	28.8	29.2	29.0	29.5	0.7
3-Methylheptane	26.4	27.9	28.5	26.0	28.8	28.6	28.7	27.0	27.2	27.3	27.6	1.0
n-Octane	27.0	28.6	29.7	30.2	29.8	29.2	29.8	28.2	29.1	29.7	29.2	1.0
n-Nonane	22.8	25.3	27.4	26.8	27.6	28.5	26.6	25.2	25.5	25.6	26.1	1.6
n-Decane	18.0	17.1	17.6	16.9	16.5	17.3	16.0	15.8	15.5	14.6	16.5	1.1

Table 5.11. Laboratory Decay Study of C_5-C_{10} Hydrocarbons; Concentrations in ppbV

Sample Number A-62	Day of Analysis										Mean	Standard Deviation
	1	5	6	9	12	16	19	23	26	30		
Isoprene	40.6	43.6	45.0	42.7	44.4		43.4	37.3	36.7	36.2	41.1	3.5
2,2-Dimethylbutane	25.4	28.7	29.5	29.4	28.4		27.8	24.9	26.7	26.9	27.5	1.7
2-Methylpentane	33.9	34.3	35.3	33.3	35.1		34.3	32.5	35.5	33.2	34.1	1.0
3-Methylpentane	45.0	47.6	48.1	49.3	48.9		47.6	44.1	46.8	48.5	47.3	1.8
1-Hexene	53.9	55.0	56.4	54.6	54.9		54.2	55.5	55.2	53.1	54.8	1.0
2-Methylpentene	97.6	98.9	100.3	99.4	100.9		97.5	93.6	95.8	96.0	97.8	2.4
2,4-Dimethylpentane	31.4	32.3	32.2	32.7	32.3		31.6	31.1	32.1	32.1	32.0	0.5
Cyclohexane	74.0	74.2	74.7	72.6	71.6		71.1	57.5	48.6	53.6	66.4	10.2
3-Methylhexane	52.6	61.6	48.4	50.6	50.6		50.0	50.1	53.3	51.9	51.0	1.5
2,2,4-Trimethylpentane	68.4	67.0	63.4	68.2	69.1		67.2	68.4	71.8	70.1	68.2	2.3
n-Heptane	43.7	43.2	40.0	43.4	43.2		42.7	41.8	43.1	42.6	42.6	1.1
Methylcyclohexane	33.9	34.0	32.2	35.5	34.7		34.1	33.9	34.7	33.8	34.1	0.9
2,3,4-Trimethylpentane	29.9	30.4	31.1	30.7	30.6		30.1	29.5	29.7	29.8	30.2	0.5
3-Methylheptane	28.6	30.1	31.2	31.5	31.6		30.2	28.3	29.2	29.1	30.0	1.3
n-Octane	28.7	29.5	30.6	30.8	30.6		30.8	28.7	29.4	30.3	29.9	0.9
n-Nonane	24.5	26.2	28.2	27.5	28.0		27.6	25.4	26.8	26.3	26.7	1.2
n-Decane	18.7	18.0	18.2	17.3	17.6		16.5	16.6	16.6	14.9	17.2	1.1

Table 5.12. Laboratory Decay Study of C_5-C_{10} Hydrocarbons; Concentrations in ppbV

Sample Number A-127	Day of Analysis										Mean	Deviation
	1	5	6	9	12	16	19	23	26	30		
Isoprene	35.6	43.7	43.5	39.0	38.4	38.0	37.0	28.8	29.2	27.9	36.1	5.8
2,2-Dimethylbutane	23.8	26.4	26.2	27.3	26.2	26.2	26.3	23.7	23.6	25.6	25.5	1.3
2-Methylpentane	30.5	32.5	32.1	30.2	31.4	31.5	32.2	30.4	32.3	30.0	31.3	1.0
3-Methylpentane	37.0	40.0	38.9	40.8	39.6	39.5	40.1	37.0	37.9	38.4	38.9	1.3
1-Hexene	44.8	47.2	46.4	45.4	44.8	44.9	45.8	46.9	46.6	44.8	45.8	0.9
2-Methylpentene	104.8	103.9	101.0	112.1	108.9	104.5	103.7	96.3	94.6	95.0	102.5	5.8
2,4-Dimethylpentane	28.6	29.8	29.3	30.3	29.5	29.4	29.6	28.5	28.8	28.4	29.2	0.6
Cyclohexane	61.9	65.4	58.9	56.5	54.5	54.7	53.0	45.9	42.0	42.5	53.5	7.9
3-Methylhexane	38.3	36.7	35.9	35.6	34.7	34.2	34.7	35.8	35.2	35.4	35.6	1.2
2,2,4-Trimethylpentane	61.3	60.1	59.3	60.4	60.0	59.0	59.7	60.6	59.5	59.5	59.9	0.7
n-Heptane	35.8	34.2	33.0	33.8	33.6	33.1	33.4	33.0	32.5	32.7	33.5	0.9
Methylcyclohexane	32.7	32.8	31.6	32.3	32.2	31.9	31.9	32.0	31.6	31.3	32.0	0.5
2,3,4-Trimethylpentane	28.0	28.8	28.6	28.8	28.6	28.3	28.5	27.4	27.5	26.9	28.1	0.7
3-Methylheptane	26.1	26.8	26.8	28.3	27.4	27.1	27.1	25.2	25.4	25.0	26.5	1.1
n-Octane	28.8	27.8	28.6	28.7	28.5	27.9	28.4	26.4	27.4	26.7	27.9	0.8
n-Nonane	24.2	33.2	26.0	25.7	26.2	25.4	25.3	22.3	23.1	24.1	25.6	3.0
n-Decane	18.3	16.8	16.9	16.5	15.7	15.4	14.6	16.0	12.8	14.5	15.7	1.5

Table 5.13. Percent Change in Concentration, Laboratory Mix C_5-C_{10} Hydrocarbons

	(Day 30 - Day 1/Day 1) x 100				(Day 30 - Mean/Mean) x 100			
	A-6	A-30	A-62	A-127	A-6	A-30	A-62	A-127
Isoprene	-14.5	-16.5	-10.8	-21.6	-10.0	-24.8	-11.9	-22.7
2,2-Dimethylbutane	2.6	5.3	5.9	7.6	0.0	- 4.1	- 2.2	0.4
2-Methylpentane	- 3.3	7.6	- 2.1	- 1.6	- 2.0	- 1.2	- 2.6	- 4.1
3-Methylpentane	6.8	14.3	7.8	3.8	3.6	3.4	2.5	- 1.3
1-Hexene	- 0.8	3.1	- 1.5	0.0	- 0.8	3.9	3.1	- 2.1
2-Methylpentene	0.2	- 6.4	- 1.6	- 9.3	- 0.6	- 7.3	- 1.8	- 7.3
2,4-Dimethylpentane	4.1	0.3	2.2	- 0.7	6.1	- 1.6	0.3	- 2.7
Cyclohexane	7.8	-22.2	-27.6	-31.3	3.4	-14.8	-19.3	-20.6
3-Methylhexane	5.9	- 5.3	- 1.3	- 7.6	5.2	- 0.5	1.8	- 0.6
2,2,4-Trimethylpentane	7.7	0.8	2.5	- 2.9	4.8	0.5	2.8	- 0.7
n-Heptane	5.3	- 7.5	- 2.5	- 8.7	3.8	- 2.8	0.0	- 2.4
Methylcyclohexane	4.2	- 5.1	- 0.3	- 4.3	2.7	- 1.2	- 0.9	- 2.2
2,3,4-Trimethylpentane	- 0.7	3.2	- 0.3	- 3.9	- 0.7	- 1.7	6.6	- 4.3
3-Methylheptane	2.4	3.4	1.7	- 4.2	- 1.1	- 1.1	- 3.0	- 5.7
n-Octane	- 0.8	10.0	5.6	- 7.3	- 0.8	1.7	1.3	- 4.3
n-Nonane	13.5	12.3	7.3	- 0.4	- 0.4	1.9	- 1.5	- 5.9
n-Decane	-19.9	-18.9	-20.3	-20.8	- 7.6	-11.5	-13.4	- 7.6
MEAN	1.2	- 1.3	- 2.2	- 6.7	0.3	- 3.7	- 2.2	- 5.5

Table 5.14. C_2-C_5 Hydrocarbons in Roadside Samples, ppbC

SAMPLE NUMBER	A-84				A-176				A-190				Mean	Standard Deviation
DATE OF COLLECTION	7/6/78 (0730-0910 EDT)				7/6/78				7/6/78					
DATE OF ANALYSIS	7/7	7/7	7/18	7/25	7/6	7/7	7/18	7/25	7/6	7/6	7/18	7/25		
Ethane	12.8	13.2	13.6	13.0	13.3	12.4	12.4	11.9	12.7	13.8	12.7	12.5	12.9	0.5
Ethylene	104.8	103.5	98.2	100.5	102.5	99.0	94.6	97.9	108.9	106.6	100.4	103.1	101.7	4.0
Propane	6.2	6.6	7.1	6.6	6.0	5.8	5.0	6.3	6.0	6.6	6.4	6.0	6.2	0.5
Acetylene	138.1	136.9	126.6	119.4	149.0	130.2	124.5	120.3	149.5	142.2	131.2	127.8	133.0	10.2
Isobutane	7.0	9.1	6.3	7.6	7.8	6.2	7.4	8.7	10.4	6.4	7.5	7.6	7.7	1.2
n-Butane	38.6	38.8	34.6	37.2	38.7	35.8	35.1	36.0	40.4	38.0	38.8	36.9	37.4	1.8
Propylene	34.3	31.3	28.6	28.6	32.3	29.5	27.0	27.7	35.8	34.1	31.3	31.2	31.0	2.8
Isopentane	65.1	59.3	58.5	56.3	62.3	60.0	55.4	55.8	61.0	61.2	55.1	59.5	59.1	3.1
Pentane	44.3	42.2	40.5	37.6	38.5	38.1	38.3	45.1	42.4	32.7	39.0	38.4	39.8	3.4
SUM	451.2	440.9	414.1	406.8	450.5	417.0	399.7	409.7	467.1	441.6	422.4	423.0	428.7	21.0
MEAN	428.2				419.2				438.5				428.6	9.7
STANDARD DEVIATION	21.2				22.0				21.0					

Table 5.15. Olefinic and Paraffinic Hydrocarbons in Roadside Samples, ppbC

SAMPLE NUMBER	A-84				A-176				A-190				Mean	Standard Deviation
DATE OF COLLECTION	7/6/78				7/6/78				7/6/78					
DATE OF ANALYSIS	7/7	7/7	7/19	7/25	7/6	7/7	7/18	7/25	7/6	7/6	7/19	7/25		
2-Pentene + Isoprene	11.3	6.5	9.8	(a)	(a)	(a)	9.9	9.1	9.8	10.3	7.9	8.9	9.3	1.4
2,2-Dimethylbutane	7.8	6.0	5.9	3.8	6.2	5.9	6.4	5.0	6.7	6.6	5.8	5.6	6.0	1.0
2-Methylpentane	25.6	22.5	26.0	22.1	20.6	21.4	19.1	21.7	20.2	21.2	21.6	21.4	21.9	2.0
3-Methylpentane	15.6	16.3	19.8	16.1	17.0	19.9	11.8	14.6	18.5	13.1	22.5	16.9	16.8	3.0
1-Hexene	— (b)	—	—	—	—	—	—	—	—	—	—	—	—	—
n-Hexane	13.3	13.7	11.8	12.7	18.0	13.0	11.6	12.4	19.0	12.4	13.2	12.1	13.6	2.4
2,4-Dimethylpentane	1.9	1.3	3.4	3.4	2.5	2.9	1.7	1.7	2.3	1.9	2.0	<0.7	2.1	0.8
Cyclohexane	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2-Methylhexane	18.2	19.2	21.6	28.9	19.6	23.5	21.5	19.7	24.1	29.6	25.1	29.4	23.4	4.1
3-Methylhexane	9.5	10.3	10.4	14.9	10.6	8.7	7.1	7.4	8.5	10.6	11.9	12.7	10.2	2.2
2,2,4-Trimethylpentane	16.6	10.7	12.0	9.9	11.7	12.0	11.8	10.1	11.7	13.1	29.3	9.8	12.1	2.1
n-Heptane	9.1	8.2	9.6	6.8	9.2	8.9	7.9	9.6	8.9	9.2	12.2	7.8	8.9	1.3
2,5-Dimethylhexane	6.4	5.7	7.1	5.6	6.8	6.1	5.2	4.8	6.5	5.9	6.9	5.6	6.0	0.7
2,3,4 Trimethylpentane	5.4	2.2	5.4	2.2	4.5	1.9	2.8	1.6	5.3	4.8	4.4	3.2	3.6	1.5
2-Methylheptane	59.4	58.8	59.7	58.5	57.9	57.9	54.2	55.0	57.8	57.4	58.0	57.3	57.7	1.6
3-Methylheptane	8.5	9.0	12.4	9.0	10.9	10.6	9.8	10.3	9.7	8.9	9.4	8.5	9.7	1.1
n-Octane	7.6	7.4	8.5	4.8	6.8	6.1	5.3	5.6	6.4	5.9	5.2	6.8	6.4	1.1
n-Nonane	12.5	11.7	12.1	11.6	11.4	11.4	10.3	10.0	12.6	11.4	12.5	10.1	11.5	0.9
n-Decane	14.2	13.0	7.2	7.3	7.1	7.5	8.2	5.0	8.3	8.8	8.9	6.6	8.5	2.6
SUM	242.9	213.5	242.7	217.6	220.8	217.7	204.6	203.6	236.3	231.1	243.2	223.4	224.8	14.3
MEAN	229.2				211.7				233.5				224.8	11.5
STANDARD DEVIATION	15.8				8.8				8.4					

(a) Peak obscured by water spike

(b) — Not detected

Table 5.16. Aromatic Hydrocarbons in Roadside Samples, ppbC

SAMPLE NUMBER	A-84				A-176				A-190				Mean	Standard Deviation
DATE OF COLLECTION	7/6/78				7/6/78				7/6/78					
DATE OF ANALYSIS	7/7	7/7	7/19	7/25	7/6	7/7	7/19	7/25	7/6	7/6	7/19	7/25		
Benzene	41.2	37.0	43.3	43.9	36.3	36.8	35.9	39.4	36.9	36.5	35.7	49.8	39.4	4.4
Toluene	49.0	47.6	53.2	48.7	49.0	48.3	49.7	46.0	51.1	51.1	58.8	56.8	50.8	3.8
Ethylbenzene	12.0	10.4	12.0	10.6	9.6	10.4	10.4	8.1	10.4	9.6	12.8	11.5	10.6	1.3
p-Xylene + α Pinene	10.4	11.2	12.0	10.6	11.2	12.0	9.6	6.1	11.2	10.4	11.2	9.5	10.4	1.6
m-Xylene	19.2	19.2	20.0	18.6	19.2	19.2	18.4	15.3	19.2	19.2	20.0	19.5	18.9	1.2
o-Xylene	12.0	12.0	11.2	10.6	12.8	11.2	11.2	9.0	13.6	9.6	12.0	10.7	11.3	1.3
n-Propylbenzene	1.8	1.8	1.8	0.9	0.9	0.9	1.8	<0.9	1.8	—	1.8	—	1.2	0.7
1,3,5-Trimethylbenzene	4.5	2.7	1.8	2.2	0.9	3.6	1.4	2.2	1.8	3.6	0.9	1.6	2.3	1.1
m-Ethyltoluene	10.8	9.9	10.8	10.0	10.8	10.8	9.9	6.8	9.9	9.9	11.7	10.6	10.2	1.2
t-Butylbenzene	—	—	—	—	—	—	—	—	—	—	—	—	—	—
o-Ethyltoluene	0.9	1.8	0.9	0.9	<0.9	0.9	0.9	<0.9	0.9	0.9	<0.9	0.9	1.0	0.3
1,2,4-Trimethylbenzene	10.8	10.8	9.0	7.8	9.9	10.8	7.2	5.2	10.8	11.7	9.9	9.7	9.5	1.9
1,2,3-Trimethylbenzene	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	0.0
n-Butylbenzene	—	—	<1.0	—	—	<1.0	<1.0	—	<1.0	—	<1.0	<1.0	0.5	0.5
SUM	173.5	165.3	177.9	165.7	162.4	166.8	158.3	140.8	169.5	163.4	177.6	182.5		
MEAN	170.6				157.1				173.3				167.0	11.0
STANDARD DEVIATION	6.2				11.4				8.5				167.0	8.7

(a)-- Not detected

compounds into evacuated stainless steel cylinders and then pressurizing with hydrocarbon-free air to a known pressure. Since the volume of the liquid compound, the cylinder volume, and the final pressure of the mixture were all accurately known, one can calculate the concentration of individual species through this formula:

$$\frac{(I)(D)(1000)}{PV} = C$$

where

I = Volume of compounds injected (μL)
D = Density of liquid compound (g/mL)
P = Final pressure (atm)
V = Volume of container (m^3)
C = concentration of compound ($\mu g/m^3$).

To convert from $\mu g/m^3$ to ppm,

$$(C_{\mu g/m^3}) \frac{(2.45 \times 10^4)}{(M \times 10^6)} = C_{ppm}$$

where

M = Molecular weight.

In both the aromatic and aliphatic standard mixtures, 200 μL of each compound were injected. Both containers were pressurized to 500 psi (34 atm).

The C_2-C_5 column was calibrated periodically with prepared mixtures from Scott Environmental Laboratories as well as with an NBS propane (0.976 ppm) mixture, SRM #1660.

In the calibration of C_2-C_5, aliphatic, and aromatic compounds, the cryogenic traps were replaced by 1-mL sample loops. The calibration mixtures did not need further concentrating, so they were injected directly from the loops at room temperature. The use of the 1-mL loop slightly affected the retention times of the compounds as compared to the cryogenic trapping procedure. Therefore, the quantitative calibrations were done with the 1-mL loops, while qualitative calibrations (peak elution times) were done with diluted mixtures on the cryogenic traps.

The quantitative calibrations were performed at monthly intervals since the responses of the FID's were not expected to change greatly. This stability was shown by the fact that very few changes in response factors were required in any of the recalibrations.

The qualitative calibrations were performed, on the average, at twice-weekly intervals. Dilutions of the standard mixtures (approximately 50 ppb) would be cryogenically trapped and analyzed to allow the C_2-C_5, aliphatic, and aromatic elution times to be checked and adjusted.

The calibrations in all cases involved analyzing the standard mixtures and entering the species concentration and/or retention time of each chromatogram peak into the computer. The computer then "manufactured" a standard chromatogram to which subsequent analyses were compared. Thus, peaks were automatically identified and quantified by their elution times and sizes.

SECTION 6.0

DATA SUMMARIES

6.1 CONTENTS OF DATA SUMMARY SECTION

This section contains summaries of pollutant and meteorological parameters from the eight ground station monitoring sites in Tulsa, Oklahoma, during the summer of 1977. Some summaries of ozone and wind data gathered by the Tulsa City/County Health Department are also given. The data summaries are divided into five categories: ozone; oxides of nitrogen and hydrocarbons; meteorological parameters; summaries of hydrocarbon species; and Tenax GC/MS results.

Individual hourly averages in SAROAD format for all pollutant and meteorological parameters are in Volume II of this report. Volume II also contains the following: annotated flight tracks of all aircraft flights; computer printout of all flight data; pibal sounding data; listings of concentrations for all individual hydrocarbon species; and a listing of all species found in Tenax cartridges by GC/MS/COMP.

6.2 OZONE DATA SUMMARIES

6.2.1 Mean Daily Ozone Concentrations

Mean daily ozone concentrations, i.e., the average of 24 hourly values each day, are given for each of the eight monitoring stations in Tables 6.1 through 6.8. The actual number of hourly observations is also listed. Mean (by month of) daily maximum (by month of) hourly ozone concentrations are given in Table 6.9. Maximum hourly ozone concentrations for each station for each month are given in Tables 6.10, 6.11, and 6.12.

6.2.2 Ozone Cumulative Frequency Distributions

Cumulative frequency distributions, or percentile values, for the 3-month period for each monitoring site are shown in Table 6.13. The percentiles shown are 10, 30, 50, 70, 95, 96, 97, 98, and 99. Also listed are the maximum value, second and third maximum values, and the arithmetic mean.

Table 6.1. Mean daily ozone concentration. July, August, September, 1977. Liberty Mounds

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	0.030	24	0.042	20	0.031	23
2	0.032	23	0.061	23	0.034	24
3	0.036	24	0.063	23	0.043	24
4	0.040	24	0.072	23	0.052	23
5	0.049	23	0.078	23	0.037	18
6	0.053	24	0.055	23	0.037	24
7	0.044	23	0.056	24	0.034	20
8	0.050	24	0.059	23	0.031	24
9	0.046	24	0.056	24	0.031	23
10	0.039	23	0.054	23	0.030	24
11	0.043	23	0.047	23	0.035	24
12	0.039	23	0.055	23	0.043	24
13	0.033	20	0.040	23	0.027	24
14	0.042	23	0.053	24	0.025	19
15	0.055	24	0.049	23	0.033	19
16	0.061	23	0.039	23	0.051	24
17	0.050	23	0.030	23	0.041	24
18	0.047	23	0.050	23	0.034	24
19	0.057	23	0.048	23	0.023	23
20	0.046	24	0.047	23	0.033	21
21	0.040	23	0.050	24	0.055	24
22	0.031	24	0.044	23	0.066	23
23	0.042	24	0.051	23	0.045	24
24	0.046	24	0.049	24	0.036	23
25	0.061	24	0.053	23	0.040	24
26	0.047	23	0.051	24	0.035	24
27	0.023	23	0.040	23	0.039	24
28	0.037	23	0.027	22	0.037	24
29	0.059	24	0.032	23	0.036	24
30	0.050	22	0.035	23	0.037	24
31	0.058	22	0.036	24		

Table 6.2. Mean daily ozone concentration. July, August, September, 1977. Tulsa Post Office

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	-	0	0.027	23	0.021	24
2	-	0	0.047	24	0.023	24
3	-	0	0.031	24	0.035	24
4	-	0	0.028	24	0.041	24
5	-	0	0.026	23	0.032	24
6	-	0	0.012	24	0.031	24
7	-	0	0.012	24	0.028	22
8	-	0	0.014	24	0.023	24
9	-	0	0.013	24	0.024	24
10	0.041	6	0.029	23	0.024	24
11	0.019	23	0.029	24	0.033	18
12	0.015	18	0.034	24	0.016	24
13	0.017	20	0.027	24	0.017	24
14	0.024	23	0.037	24	0.022	24
15	0.035	13	0.025	24	0.021	24
16	0.045	23	0.016	24	0.019	24
17	0.035	24	0.017	24	0.014	24
18	0.029	23	0.030	24	0.016	24
19	0.047	24	0.020	24	0.019	24
20	0.042	23	0.031	24	0.025	24
21	0.024	24	0.030	24	0.030	24
22	0.051	23	0.025	24	0.047	24
23	0.054	24	0.041	24	0.015	24
24	0.029	23	0.034	24	0.021	24
25	0.049	23	0.033	24	0.032	24
26	0.039	23	0.012	24	0.018	23
27	0.021	24	0.011	24	0.030	24
28	0.042	23	0.015	23	0.022	24
29	0.050	20	0.026	23	0.025	14
30	0.029	24	0.024	24	-	0
31	0.041	23	0.017	24		

Table 6.3. Mean daily ozone concentration. July, August, September, 1977. Tulsa City/County Health Department

	July		August		September	
Date	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	-	0	0.026	24	0.025	24
2	-	0	0.053	22	0.029	24
3	-	0	0.051	23	0.036	24
4	0.050	15	0.049	23	0.049	23
5	0.047	15	0.058	23	0.031	24
6	-	0	0.042	22	0.031	24
7	-	0	0.048	24	0.029	24
8	0.037	6	0.048	23	0.031	24
9	0.033	23	0.049	23	0.033	23
10	0.040	14	0.051	23	0.026	23
11	0.045	15	0.033	23	0.031	24
12	0.036	18	0.040	21	0.038	24
13	0.032	23	0.029	23	0.021	24
14	0.043	23	0.039	24	0.025	23
15	0.052	23	0.039	23	0.022	24
16	0.054	24	0.029	14	0.036	24
17	0.052	24	0.021	13	0.035	24
18	0.045	24	0.037	23	0.033	24
19	0.053	23	0.037	23	0.022	23
20	0.045	24	0.029	23	0.027	24
21	0.037	23	0.032	24	0.050	23
22	0.049	23	0.028	23	0.067	1
23	0.054	24	0.047	23	-	0
24	0.049	18	0.036	23	-	0
25	0.052	13	0.038	24	0.048	17
26	0.040	14	0.039	24	0.024	24
27	0.020	24	0.030	23	0.028	23
28	0.041	22	0.021	24	0.020	23
29	0.060	23	0.022	23	0.022	23
30	0.046	23	0.023	23	0.012	8
31	0.042	24	0.029	24		

Table 6.4. Mean daily ozone concentration. July, August, September, 1977. Sperry

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	-	0	0.026	24	0.027	24
2	-	0	0.044	24	0.032	24
3	-	0	0.049	24	0.041	24
4	0.047	9	0.055	24	0.041	24
5	0.049	24	0.067	24	0.036	24
6	0.051	24	0.049	24	0.037	24
7	0.050	23	0.045	24	0.039	24
8	0.042	23	0.046	24	0.035	24
9	0.042	24	0.045	24	0.034	23
10	0.048	24	0.052	24	0.037	18
11	0.045	23	0.032	23	0.037	19
12	0.044	23	0.034	24	0.039	24
13	0.041	19	0.025	24	0.028	24
14	0.052	21	0.040	24	0.022	16
15	0.043	12	0.041	24	0.024	24
16	0.057	22	0.040	24	0.040	24
17	0.047	23	0.029	24	0.040	24
18	0.045	23	0.043	24	0.033	24
19	0.054	24	0.026	24	0.023	24
20	0.053	24	0.042	24	0.026	24
21	0,046	23	0.027	24	0.049	24
22	0,047	23	0.043	24	0.057	24
23	0,047	24	0.052	24	0.037	24
24	0,052	24	0,044	24	0.028	24
25	0,064	24	0.041	21	0.034	24
26	0.042	24	0,041	24	0.028	23
27	0,023	19	0.035	24	0.037	24
28	0,011	8	0.030	24	0.025	24
29	0.061	15	0.026	24	0.028	24
30	0.052	24	0.026	24	0.029	24
31	0.042	24	0.031	24		

Table 6.5. Mean daily ozone concentration. July, August, September, 1977. Skiatook Lake

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	0.054	23	0.025	22	0.029	24
2	0.044	23	0.052	24	0.027	24
3	0.043	21	0.053	24	0.030	24
4	0.045	3	0.069	24	0.036	24
5	-	0	0.079	24	0.033	24
6	0.045	4	0.054	10	0.037	23
7	-	0	-	0	0.032	24
8	-	0	-	0	0.031	24
9	0.046	10	0.049	9	0.030	23
10	0.039	24	0.052	23	0.039	24
11	0.041	22	0.036	22	0.034	23
12	0.034	22	0.034	24	0.049	24
13	0.025	22	0.026	24	0.030	24
14	0.029	22	0.040	24	0.033	24
15	0.035	23	0.046	24	0.028	24
16	0.048	22	0.041	24	0.045	23
17	0.036	24	0.030	24	0.044	24
18	0.034	23	0.043	24	0.037	24
19	0.045	23	0.029	24	0.023	24
20	0.038	22	0.037	24	0.027	24
21	0.038	21	0.025	24	0.060	24
22	0.047	23	0.039	24	0.062	23
23	0.042	24	0.037	24	0.046	24
24	0.049	24	0.044	24	0.028	24
25	0.064	23	0.037	24	0.037	34
26	0.043	24	0.041	24	0.036	24
27	0.031	24	0.033	23	0.045	24
28	0.043	24	0.029	24	0.030	24
29	0.042	24	0.021	23	0.037	23
30	0.045	24	0.023	24	0.037	24
31	0.035	24	0.033	24		

Table 6.6. Mean daily ozone concentration. July, August, September, 1977. Vera

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	0.031	24	0.034	23	0.031	24
2	0.022	23	0.048	23	0.036	24
3	0.026	24	0.059	23	0.049	24
4	0.027	21	0.058	23	0.043	24
5	0.031	21	0.067	23	0.033	24
6	0.039	24	0.053	23	0.034	24
7	0.041	23	0.052	24	0.042	23
8	0.039	23	0.048	23	0.040	21
9	0.033	24	0.049	23	0.029	24
10	0.049	23	0.052	21	0.036	24
11	0.046	23	0.036	23	0.035	24
12	0.037	23	0.040	23	0.044	24
13	0.034	22	0.033	24	0.033	23
14	0.057	21	0.045	23	0.033	24
15	0.060	23	0.038	23	0.027	24
16	0.063	23	0.035	23	0.039	24
17	0.054	24	0.028	24	0.037	24
18	0.044	23	0.041	23	0.036	24
19	0.054	23	0.034	24	0.031	24
20	0.054	23	0.042	23	0.030	24
21	0.044	23	0.027	24	0.051	23
22	0.051	23	0.038	23	0.064	24
23	0.054	23	0.052	23	0.042	24
24	0.053	24	0.050	24	0.036	24
25	0.069	23	0.042	23	0.041	24
26	0.042	23	0.044	24	0.037	24
27	0.029	23	0.037	21	0.043	24
28	0.059	23	0.029	24	0.034	24
29	0.058	21	0.025	24	0.033	24
30	0.064	22	0.029	24	0.032	23
31	0.048	24	0.029	24		

Table 6.7. Mean daily ozone concentration. July, August, September, 1977. Wynona

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	0.058	24	0.043	24	0.034	24
2	0.047	23	0.068	24	0.035	24
3	0.052	22	0.072	24	0.044	24
4	0.045	1	0.074	23	0.038	24
5	-	0	0.076	24	0.040	24
6	0.054	8	0.057	24	0.035	24
7	0.045	23	0.056	24	0.039	24
8	0.039	24	0.055	24	0.035	23
9	0.032	23	0.054	24	0.028	24
10	0.035	24	0.053	24	0.036	24
11	0.043	23	0.037	23	0.033	24
12	0.042	22	0.039	24	0.044	24
13	0.033	23	0.037	24	0.032	24
14	0.040	22	0.046	24	0.034	24
15	0.040	9	0.052	24	0.029	24
16	-	0	0.043	24	0.048	24
17	-	0	0.037	24	0.048	24
18	-	0	0.046	24	0.039	24
19	0.071	21	0.040	24	0.025	24
20	0.059	22	0.047	24	0.032	24
21	0.043	24	0.040	24	0.058	24
22	0.062	24	0.052	24	0.064	24
23	0.058	23	0.050	24	0.047	24
24	0.065	24	0.050	24	0.035	24
25	0.082	24	0.044	24	0.040	24
26	0.052	24	0.052	24	0.040	24
27	0.044	24	0.041	24	0.041	23
28	0.054	24	0.035	23	0.030	24
29	0.061	24	0.028	24	0.035	24
30	0.064	22	0.028	24	0.037	24
31	0.047	24	0.032	24		

Table 6.8. Mean daily ozone concentration. July, August, September, 1977. Ochelata

Date	July		August		September	
	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations	Mean Daily O_3 Conc., ppm	Number of Hourly Observations
1	-	0	0.034	23	0.037	24
2	-	0	0.042	14	0.037	24
3	-	0	0.074	15	0.045	24
4	-	0	0.062	23	0.045	24
5	-	0	0.071	23	0.040	24
6	0.063	11	0.054	23	0.040	24
7	0.055	23	0.047	23	0.051	24
8	0.050	23	0.046	24	0.052	24
9	0.045	24	0.048	20	0.031	23
10	0.049	23	0.048	24	0.034	22
11	0.046	23	0.032	23	0.034	24
12	0.046	22	0.037	23	0.043	24
13	0.040	23	0.030	24	0.034	24
14	0.045	23	0.044	24	0.033	24
15	0.055	20	0.041	24	0.028	23
16	0.055	23	0.038	21	0.049	23
17	0.052	24	0.031	24	0.043	24
18	0.047	23	0.041	23	0.040	24
19	0.054	23	0.031	24	0.032	24
20	0.051	23	0.045	24	0.035	24
21	0.052	23	0.036	24	0.053	24
22	0.054	23	0.047	24	0.064	23
23	0.052	23	0.048	24	0.044	24
24	0.051	24	0.045	23	0.039	24
25	0.064	23	0.042	24	0.046	24
26	0.042	23	0.040	24	0.039	24
27	0.033	23	0.035	24	0.045	23
28	0.048	21	0.029	24	0.028	24
29	0.049	23	0.024	23	0.038	24
30	0.036	13	0.029	22	0.036	24
31	0.043	11	0.029	22		

Table 6.9. Mean daily maximum hourly ozone concentrations

Site	July	Number of Days	August	Number of Days	September	Number of Days
Liberty Mounds	0.069	31	0.077	31	0.061	30
Public Health Dept.	0.074	26	0.066	31	0.061	26
Post Office - Tulsa	0.067	22	0.053	31	0.049	29
Sperry	0.079	28	0.073	31	0.062	30
Skiatook Lake	0.064	28	0.069	29	0.065	30
Vera Post Office	0.091	31	0.073	31	0.065	30
Ochelata	0.079	26	0.068	31	0.067	28
Wynona	0.075	27	0.075	31	0.063	30
Mohawk Blvd. [a]	0.087	31	0.076	31	0.075	30
Apache Street [a]	0.089	31	0.079	31	0.065	29

[a] Concentrations may be at least 20 percent higher than the other sites due to differences in calibration via NBKI procedure.

Table 6.10. Maximum hourly ozone concentrations, ppm. July, 1977

Hour, CST	Liberty Mounds	Post Office	Health Dept.	Sperry	Skiatook Lake	Vera	Wynona	Ochelata
00	0.068	0.051	0.048	0.058	0.056	0.053	0.059	0.065
01	0.068	0.049	0.049	0.052	0.056	0.048	0.058	0.063
02	0.060	0.045	0.046	0.052	0.057	0.044	0.057	0.066
03	0.058	0.043	0.045	0.052	0.058	0.035	0.052	0.073
04	0.053	0.048	0.048	0.052	0.050	0.045	0.052	0.070
05	0.043	0.045	0.043	0.047	0.051	0.035	0.047	0.078
06	0.043	0.035	0.043	0.042	0.049	0.036	0.047	0.078
07	0.050	0.030	0.048	0.049	0.047	0.043	0.052	0.090
08	0.060	0.055	0.055	0.073	0.055	0.056	0.062	0.108
09	0.073	0.072	0.080	0.091	0.059	0.075	0.074	0.118
10	0.083	0.075	0.121	0.101	0.091	0.123	0.085	0.133
11	0.089	0.092	0.119	0.099	0.080	0.135	0.092	0.143
12	0.086	0.105	0.104	0.106	0.081	0.128	0.091	0.146
13	0.086	0.127	0.124	0.110	0.081	0.135	0.101	0.146
14	0.089	0.107	0.124	0.094	0.092	0.125	0.101	0.158
15	0.091	0.100	0.102	0.087	0.091	0.114	0.091	0.158
16	0.124	0.090	0.096	0.091	0.078	0.115	0.096	0.158
17	0.127	0.090	0.090	0.094	0.082	0.116	0.089	0.158
18	0.117	0.112	0.092	0.088	0.091	0.111	0.084	0.143
19	0.091	0.087	0.063	0.088	0.085	0.095	0.081	0.123
20	0.073	0.076	0.058	0.074	0.078	0.080	0.069	0.113
21	0.070	0.064	0.055	0.064	0.068	0.064	0.064	0.112
22	0.070	0.055	0.055	0.063	0.061	0.063	0.057	0.098
23	0.069	0.052	0.048	0.058	0.056	0.062	0.059	0.088

Table 6.11. Maximum hourly ozone concentrations, ppm. August, 1977

Hour, CST	Liberty Mounds	Post Office	Health Dept.	Sperry	Skiatook Lake	Vera	Wynona	Ochelata
00	0.078	0.031	0.062	0.070	0.076	0.058	0.079	0.061
01	0.072	0.035	0.072	0.064	0.073	0.059	0.076	0.060
02	0.068	0.044	0.072	0.060	0.067	0.054	0.074	0.062
03	0.064	0.036	0.075	0.056	0.063	0.048	0.072	0.061
04	0.050	0.033	0.073	0.051	0.057	0.053	0.068	0.053
05	0.051	0.028	0.074	0.043	0.055	0.054	0.069	0.054
06	0.073	0.023	0.068	0.039	0.056	0.049	0.059	0.051
07	0.050	0.027	0.062	0.041	0.047	0.045	0.054	0.044
08	0.062	0.050	0.052	0.054	0.062	0.054	0.063	0.049
09	0.072	0.051	0.054	0.075	0.074	0.059	0.068	0.084
10	0.093	0.065	0.077	0.115	0.080	0.098	0.093	0.094
11	0.106	0.082	0.093	0.102	0.087	0.099	0.099	0.091
12	0.105	0.085	0.107	0.107	0.106	0.103	0.106	0.099
13	0.104	0.080	0.111	0.135	0.112	0.128	0.111	0.114
14	0.108	0.085	0.096	0.100	0.120	0.151	0.108	0.114
15	0.114	0.084	0.087	0.103	0.111	0.133	0.115	0.106
16	0.102	0.080	0.081	0.103	0.107	0.104	0.121	0.101
17	0.106	0.101	0.085	0.108	0.101	0.103	0.113	0.096
18	0.117	0.096	0.086	0.093	0.096	0.089	0.105	0.089
19	0.100	0.087	0.058	0.075	0.085	0.068	0.099	0.077
20	0.085	0.070	0.046	0.069	0.077	0.061	0.082	0.061
21	0.075	0.050	0.074	0.055	0.074	0.054	0.072	0.053
22	0.078	0.044	0.058	0.064	0.075	0.054	0.071	0.056
23	0.081	0.035	0.063	0.073	0.076	0.056	0.075	0.059

Table 6.12. Maximum hourly ozone concentrations, ppm. September, 1977

Hour, CST	Liberty Mounds	Post Office	Health Dept.	Sperry	Skiatook Lake	Vera	Wynona	Ochelata
00	0.073	0.050	0.067	0.067	0.079	0.068	0.076	0.064
01	0.070	0.058	0.043	0.061	0.076	0.064	0.071	0.065
02	0.066	0.052	0.042	0.061	0.069	0.061	0.067	0.062
03	0.061	0.046	0.041	0.059	0.064	0.056	0.065	0.060
04	0.058	0.050	0.045	0.052	0.061	0.055	0.060	0.058
05	0.056	0.042	0.043	0.044	0.055	0.051	0.057	0.055
06	0.051	0.037	0.042	0.035	0.054	0.063	0.060	0.052
07	0.051	0.031	0.035	0.031	0.053	0.050	0.054	0.050
08	0.063	0.033	0.046	0.042	0.061	0.046	0.055	0.052
09	0.075	0.050	0.067	0.075	0.070	0.066	0.066	0.068
10	0.079	0.063	0.082	0.095	0.078	0.086	0.075	0.083
11	0.080	0.061	0.094	0.089	0.086	0.098	0.075	0.094
12	0.076	0.067	0.086	0.094	0.080	0.095	0.080	0.102
13	0.075	0.076	0.085	0.117	0.081	0.126	0.075	0.101
14	0.081	0.075	0.093	0.098	0.085	0.118	0.075	0.108
15	0.080	0.069	0.086	0.083	0.085	0.096	0.075	0.095
16	0.079	0.067	0.066	0.080	0.080	0.083	0.075	0.089
17	0.089	0.081	0.064	0.075	0.072	0.086	0.098	0.080
18	0.081	0.079	0.050	0.076	0.074	0.085	0.077	0.086
19	0.079	0.076	0.060	0.068	0.072	0.076	0.069	0.078
20	0.079	0.070	0.073	0.064	0.071	0.071	0.067	0.065
21	0.079	0.070	0.072	0.069	0.080	0.070	0.069	0.069
22	0.079	0.051	0.069	0.065	0.081	0.061	0.077	0.069
23	0.074	0.057	0.067	0.071	0.079	0.065	0.080	0.064

Table 6.13. Percentile values, maximum values, and arithmetic mean for ozone, ppm. July - September, 1977

Monitoring Site	Percentile										Max	2nd Max	3rd Max	Arith Mean
	10	30	50	70	90	95	96	97	98	99				
Liberty Mounds	0.019	0.032	0.043	0.055	0.071	0.079	0.081	0.083	0.086	0.093	0.127	0.124	0.117	0.044
Tulsa Post Office	0.005	0.015	0.023	0.035	0.055	0.065	0.068	0.072	0.077	0.085	0.127	0.112	0.107	0.028
Tulsa City/County Health Department	0.014	0.024	0.034	0.045	0.065	0.074	0.077	0.082	0.087	0.093	0.124	0.124	0.121	0.031
Sperry	0.012	0.026	0.037	0.052	0.072	0.080	0.083	0.088	0.092	0.098	0.135	0.117	0.115	0.040
Skiatook Lake	0.011	0.027	0.038	0.050	0.067	0.075	0.076	0.080	0.086	0.092	0.120	0.112	0.112	0.039
Vera	0.015	0.027	0.036	0.050	0.075	0.090	0.094	0.098	0.104	0.115	0.151	0.135	0.135	0.042
Wynona	0.021	0.033	0.044	0.056	0.073	0.084	0.087	0.090	0.095	0.102	0.123	0.121	0.121	0.046
Ochelata	0.020	0.030	0.040	0.054	0.069	0.079	0.084	0.086	0.089	0.096	0.114	0.114	0.108	0.043
Mohawk Blvd. a/	0.005	0.025	0.038	0.056	0.083	0.093	0.096	0.099	0.105	0.110	0.142	0.133	0.128	0.042
Apache St. a/	0.013	0.028	0.041	0.055	0.078	0.089	0.092	0.097	0.107	0.120	0.166	0.166	0.163	0.043

a/ Concentrations at this site are 20 percent higher than the other sites as they are based on calibration via NBKI procedure.

6.2.3 Frequency Distribution Plots

Frequency distributions of hourly ozone concentrations for each of the eight monitoring stations are shown in a series of thirty-two bargraph figures. Ozone concentrations are displayed in increments of 0.01 ppm. The actual incremental steps are: 0.00 - 0.009; 0.01 - 0.019; 0.01 - 0.029, 0.03 - 0.039, etc. Both the number of hourly observations and the percentage of the total observations are denoted on the figures. The figures present frequency distributions for each site for each month and for the entire 3-month period.

Figures 6.1 through 6.8 are ozone frequency distributions for July 1977; Figures 6.9 through 6.16 are ozone frequency distributions for August 1977; Figures 6.17 through 6.24 are for September 1977; Figures 6.25 through 6.32 are frequency distributions for the entire 3-month period.

6.2.4 Mean Hourly Standard Deviation of Ozone Concentrations

Table 6.14 presents the mean hourly standard deviations for ozone concentrations and number of values by hour for the entire sampling period for each monitoring site.

6.2.5 Percentage of Hourly Ozone Values >0.08 ppm

Table 6.15 lists each monitoring site and gives the number of hours and percentage of all hours that exceeded a concentration of 0.08 ppm for each month and for the 3-month period.

6.2.6 Diurnal Plots of Mean Ozone Hourly Concentrations

Mean diurnal ozone concentrations for the entire period of study are plotted in Figure 6.33 for the Liberty Mounds, Tulsa Health Department, and Tulsa Post Office monitoring sites. This allows comparison of the background ozone diurnal pattern and the in-city patterns. Figure 6.34 illustrates the mean diurnal ozone concentration pattern at the Sperry, Skiatook Lake, and Wynona sites. Figure 6.35 shows the same information for the Vera and Ochelata sites.

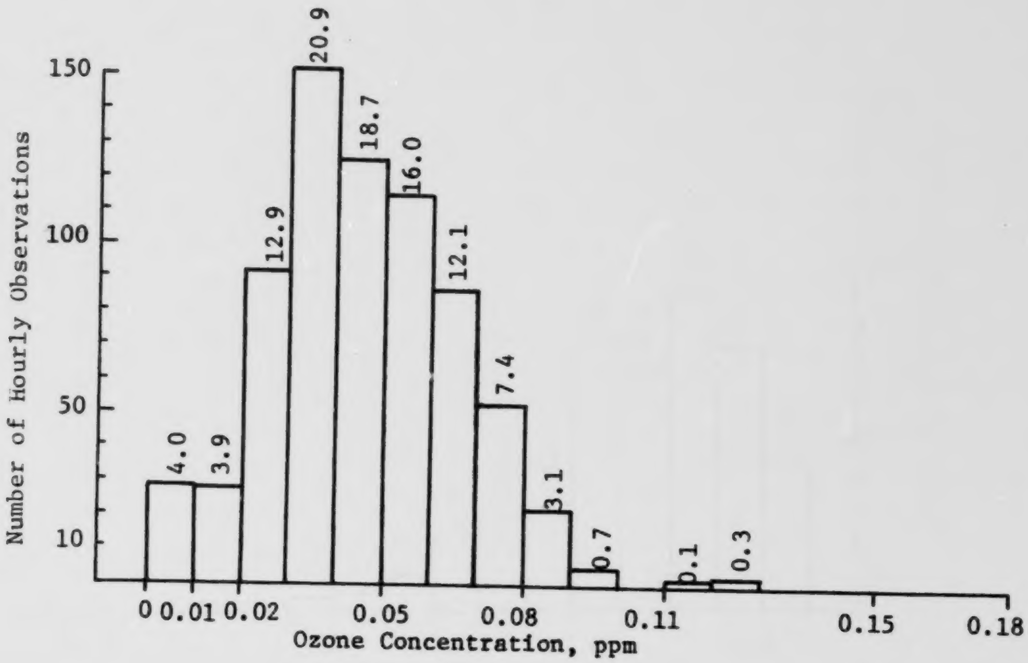

Figure 6.1. Frequency distribution of hourly ozone concentrations, Liberty Mounds. July, 1977.

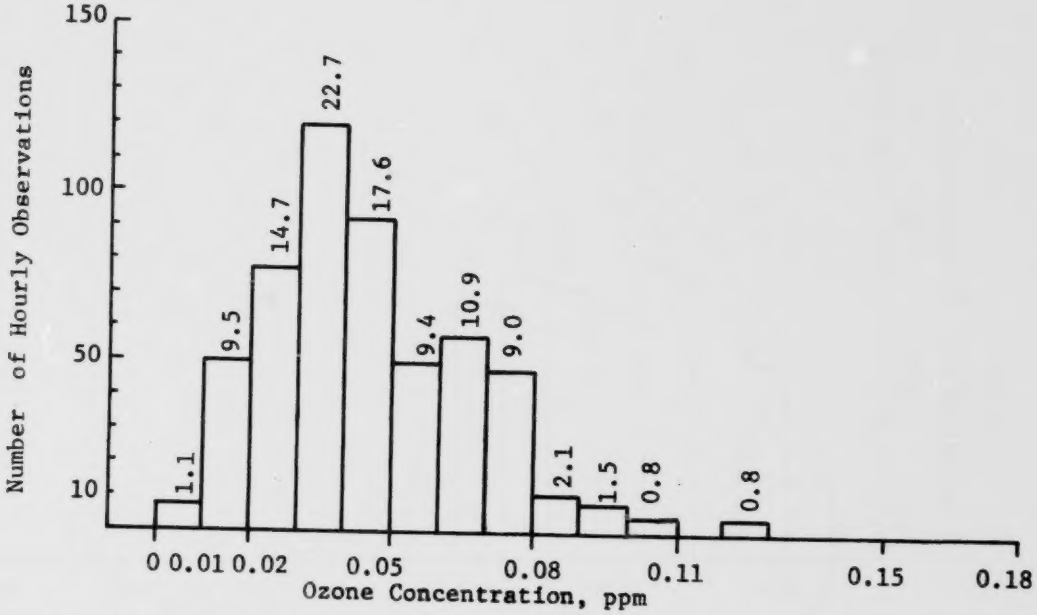

Figure 6.2. Frequency distribution of hourly ozone concentrations, Health Department. July 1977.

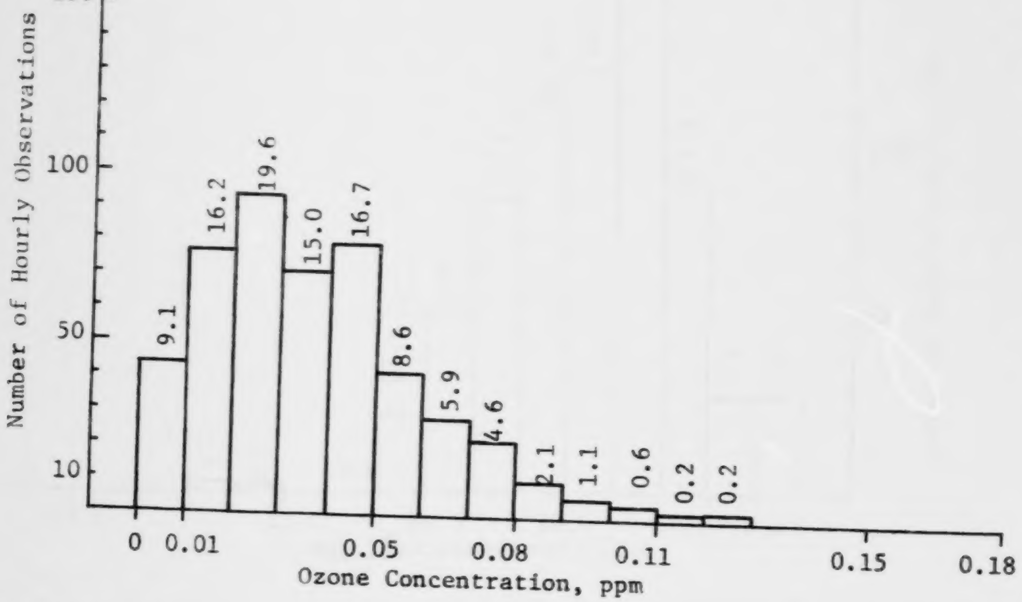

Figure 6.3. Frequency distribution of hourly ozone concentrations, Tulsa Post Office. July, 1977.

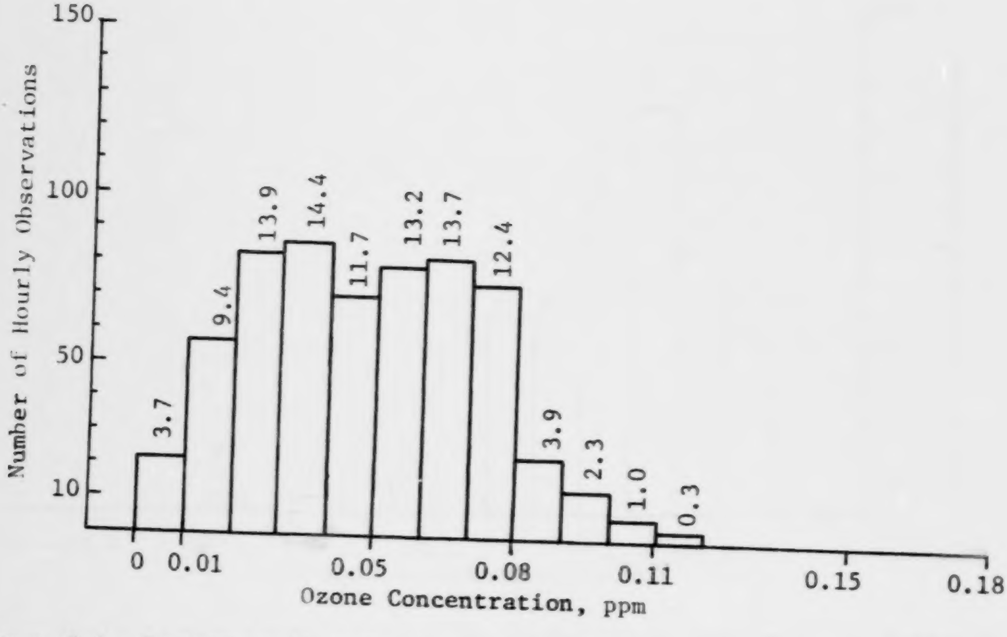

Figure 6.4. Frequency distributions of hourly ozone concentrations, Sperry. July, 1977.

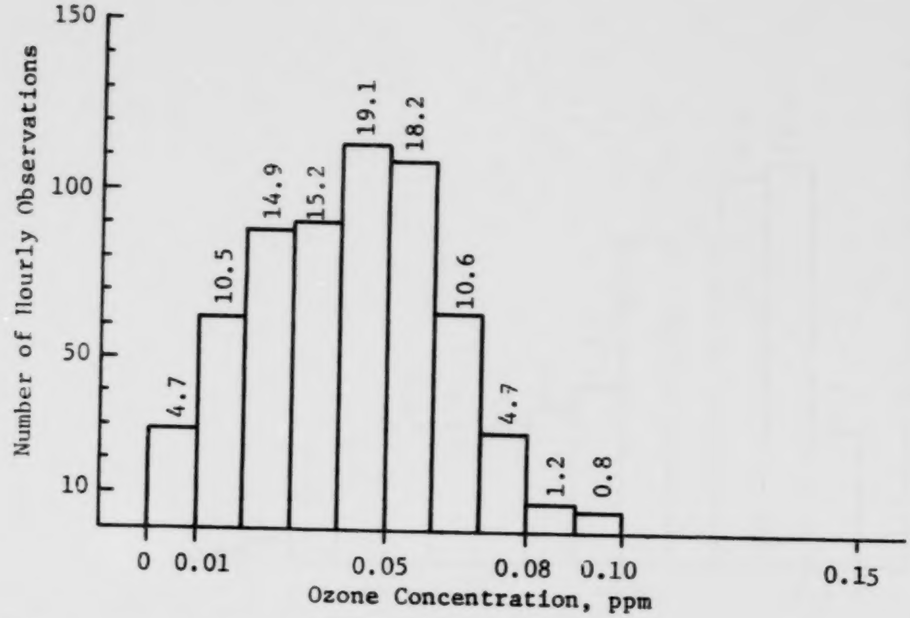

Figure 6.5. Frequency distribution of hourly ozone concentrations, Skiatook Lake. July, 1977.

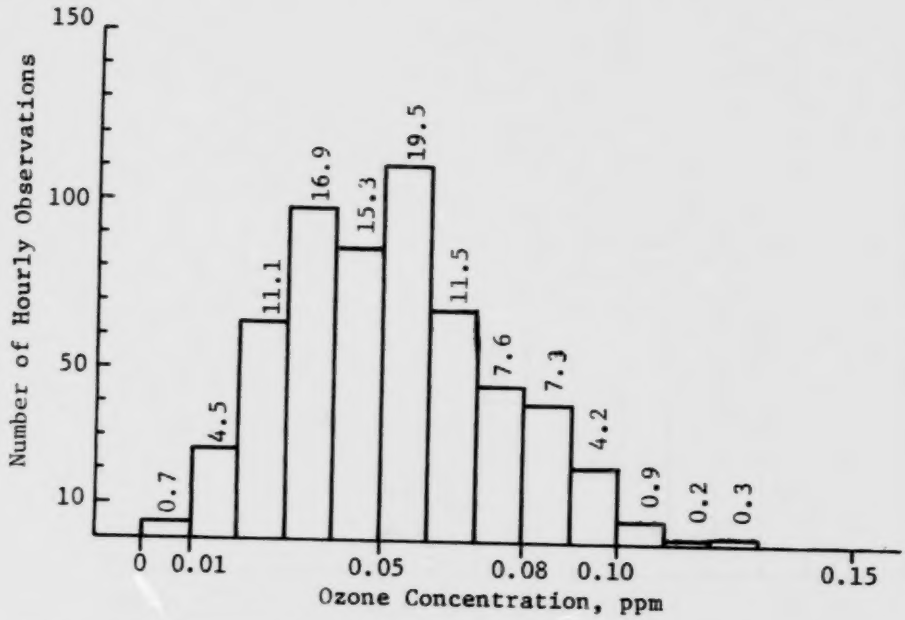

Figure 6.6. Frequency distribution of hourly ozone concentrations, Wynona. July, 1977.

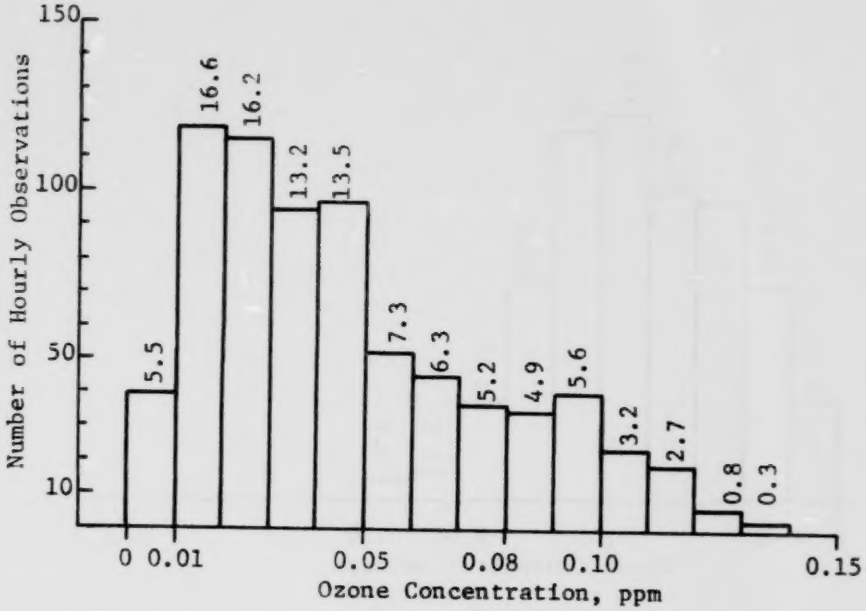

Figure 6.7. Frequency distribution of hourly ozone concentrations, Vera. July, 1977.

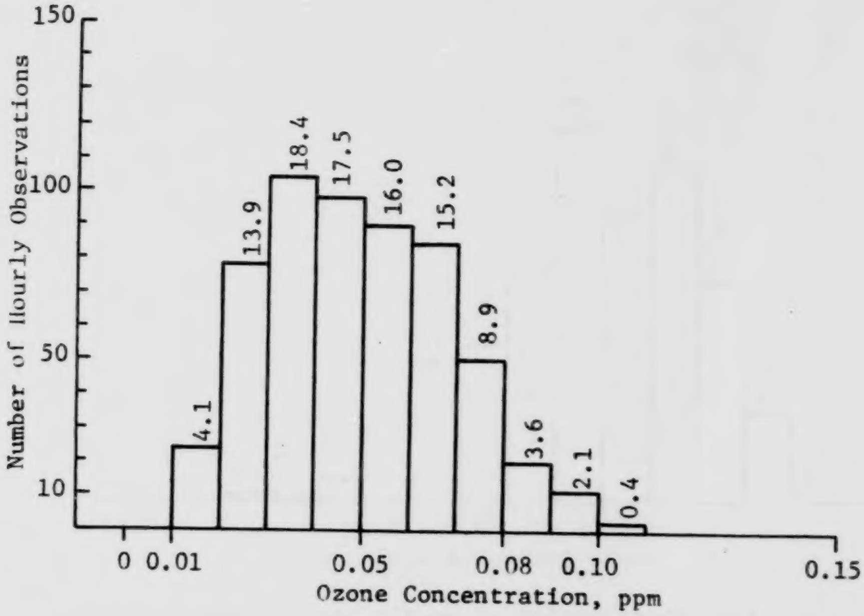

Figure 6.8. Frequency distribution of hourly ozone concentrations, Ochelata. July, 1977.

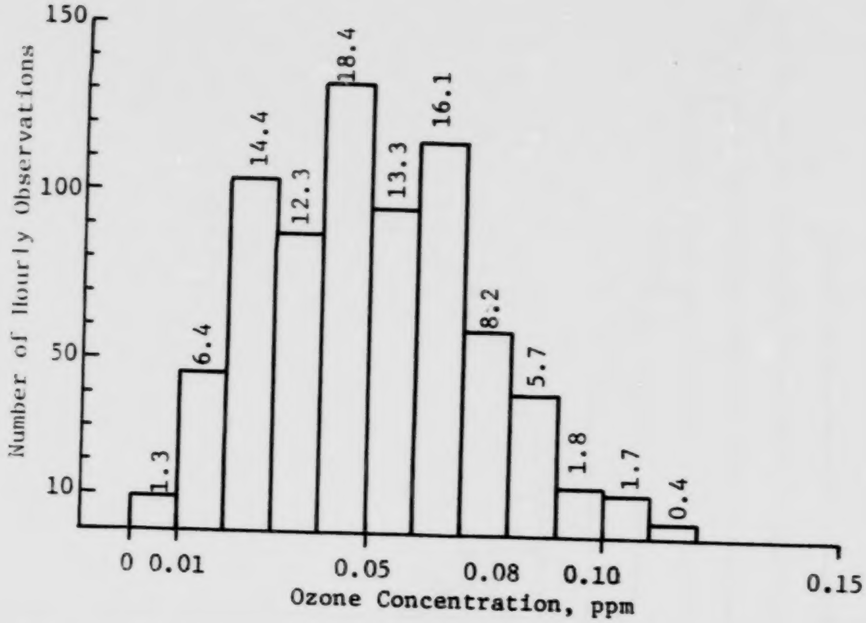

Figure 6.9. Frequency distribution of hourly ozone concentrations, Liberty Mounds. August, 1977.

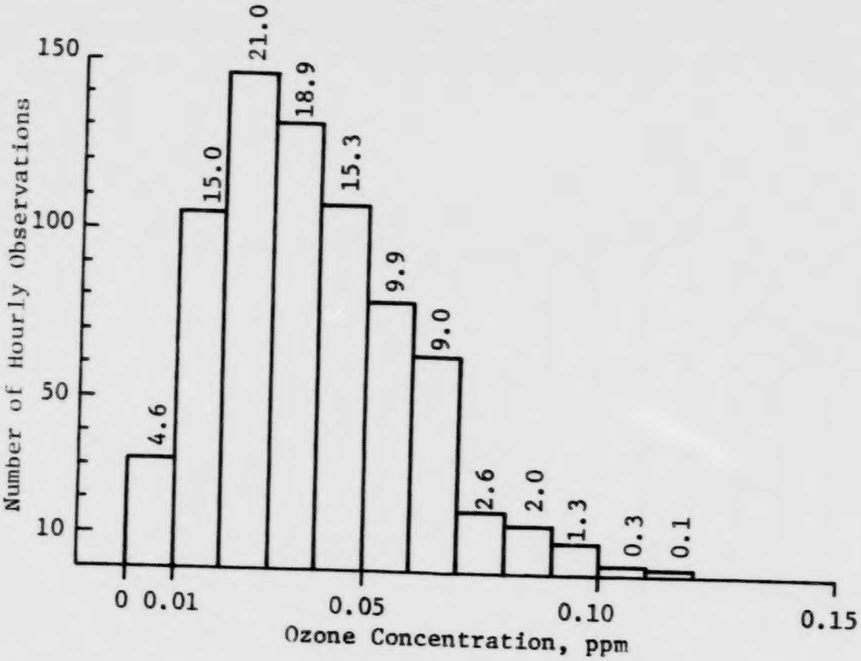

Figure 6.10. Frequency distribution of hourly ozone concentrations, Tulsa City/County Health Department. August, 1977.

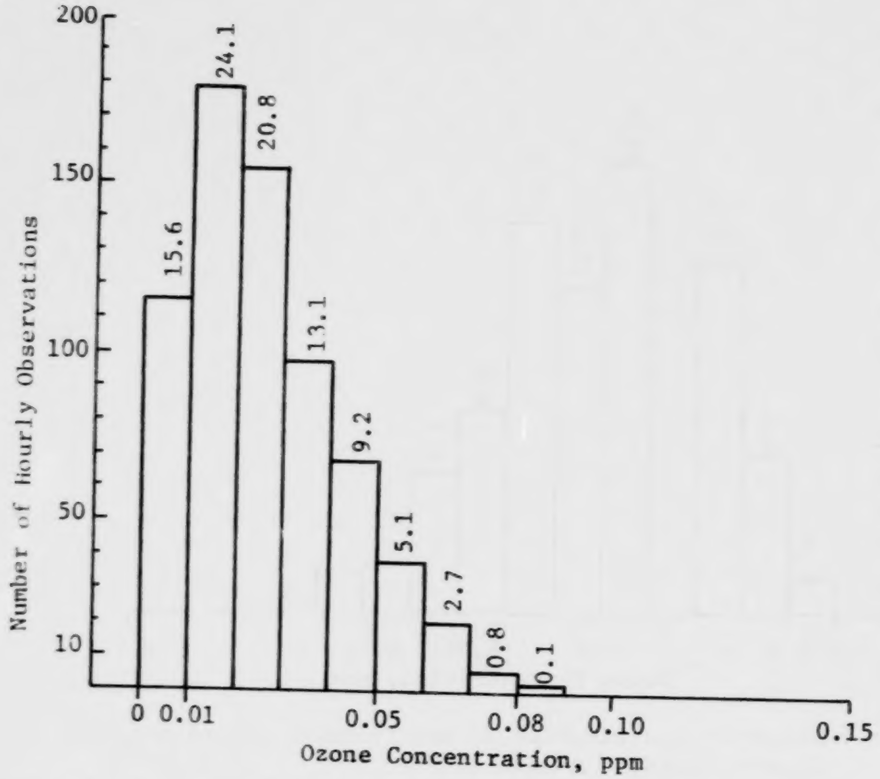

Figure 6.11. Frequency distribution of hourly ozone concentrations, Tulsa Post Office. August, 1977.

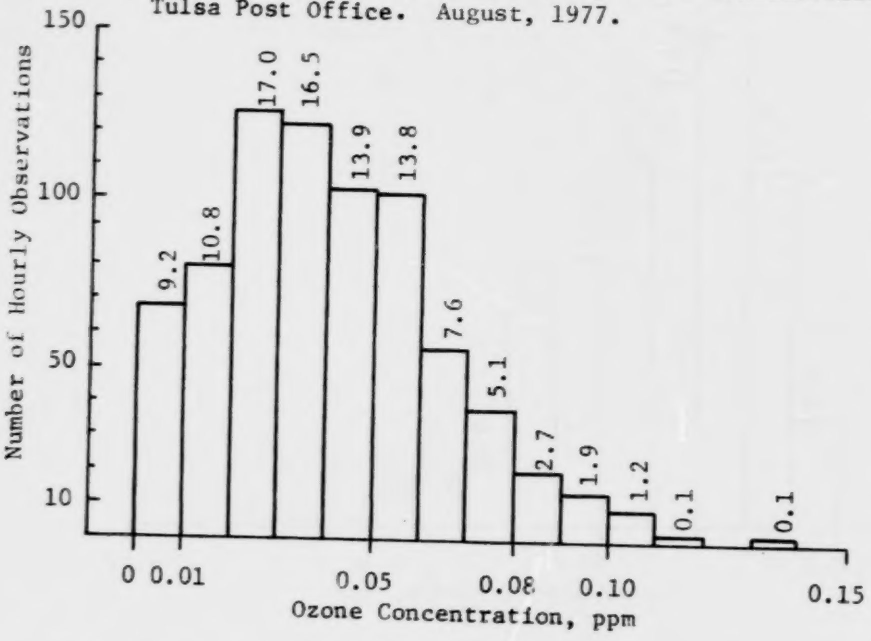

Figure 6.12. Frequency distribution of hourly ozone concentrations, Sperry. August, 1977.

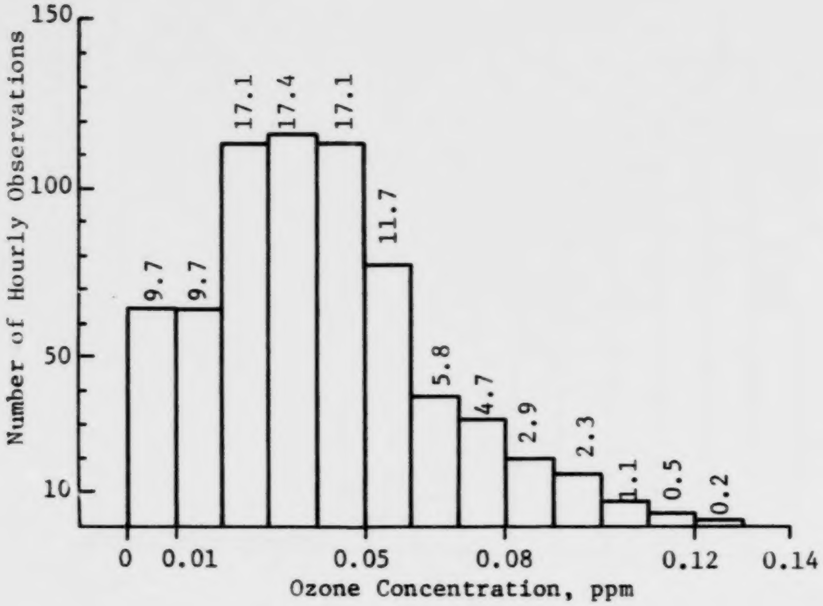

Figure 6.13. **Frequency distribution** of hourly ozone concentrations, **Skiatook Lake.** August, 1977.

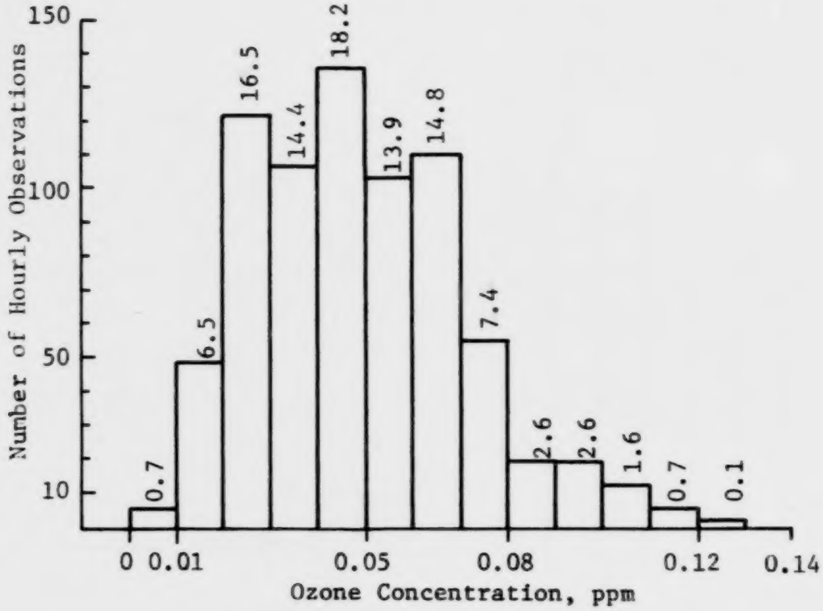

Figure 6.14. **Frequency distribution** of hourly ozone concentrations, **Wynona.** August, 1977.

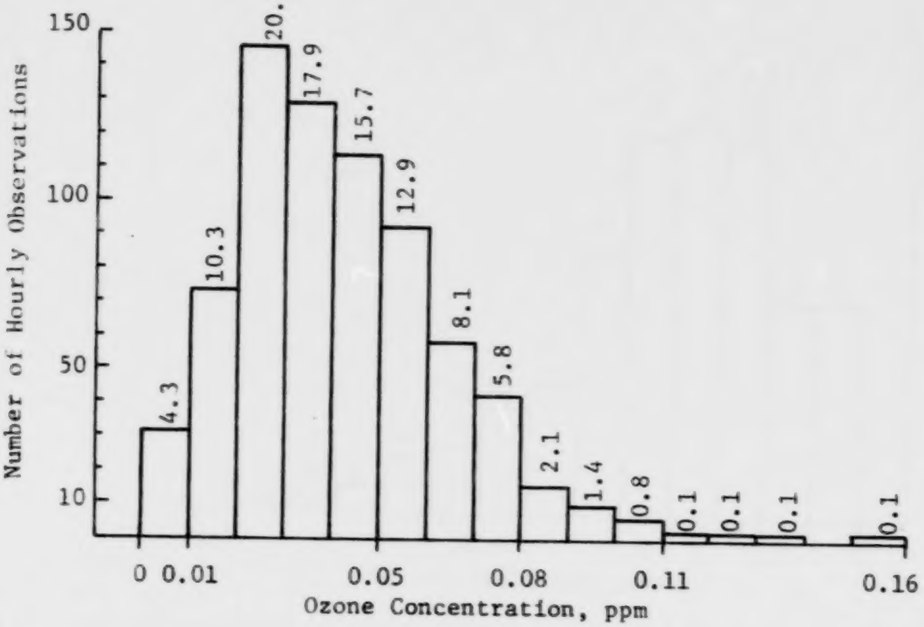

Figure 6.15. **Frequency distribution of hourly ozone concentrations, Vera.** August, 1977.

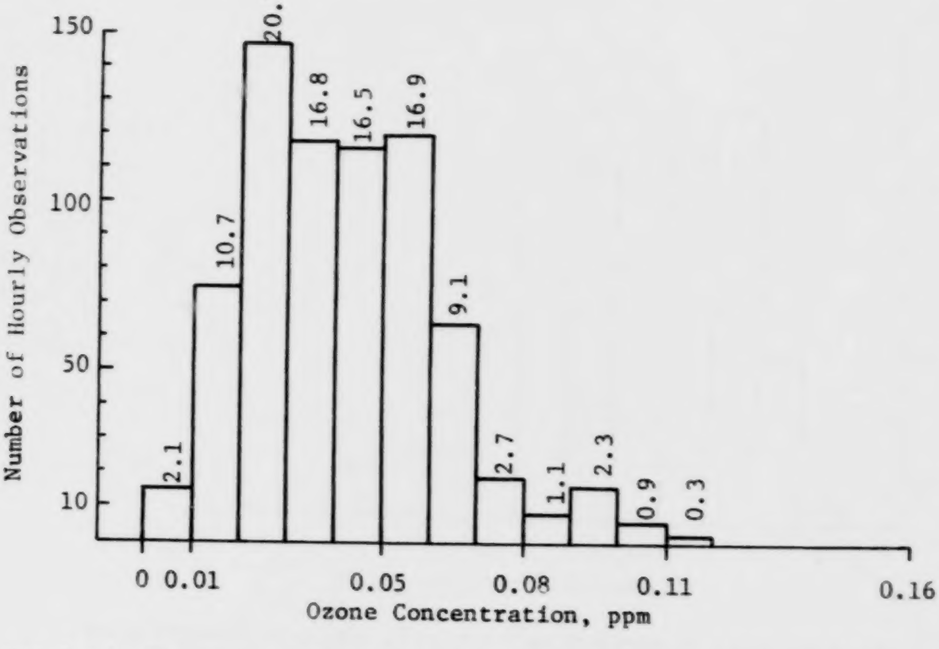

Figure 6.16. **Frequency distribution of hourly ozone concentrations, Ochelata.** August, 1977.

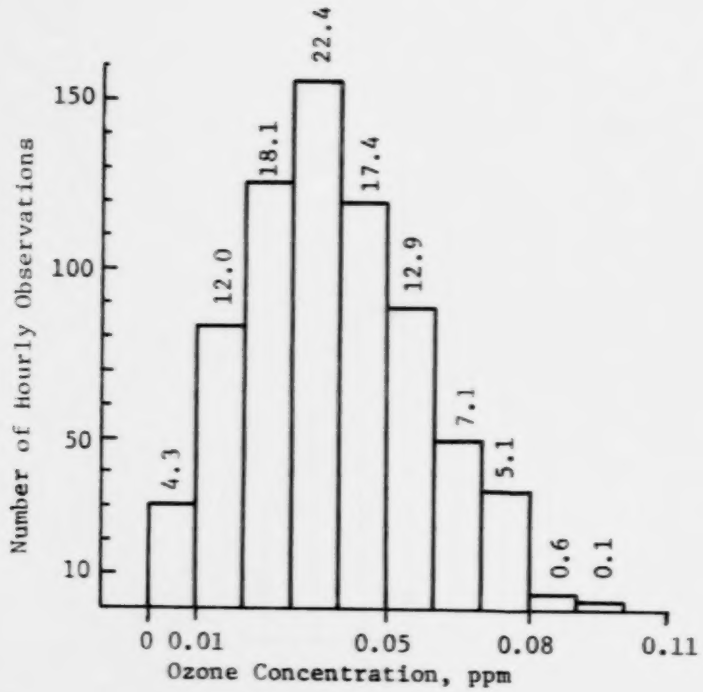

Figure 6.17. Frequency distribution of hourly ozone concentrations, Liberty Mounds. September, 1977.

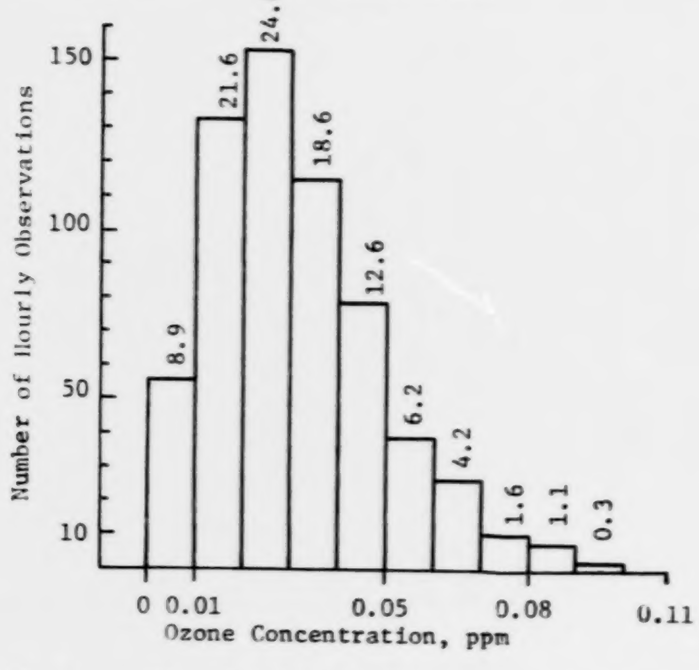

Figure 6.18 Frequency distribution of hourly ozone concentrations, Tulsa City/County Health Department. September, 1977.

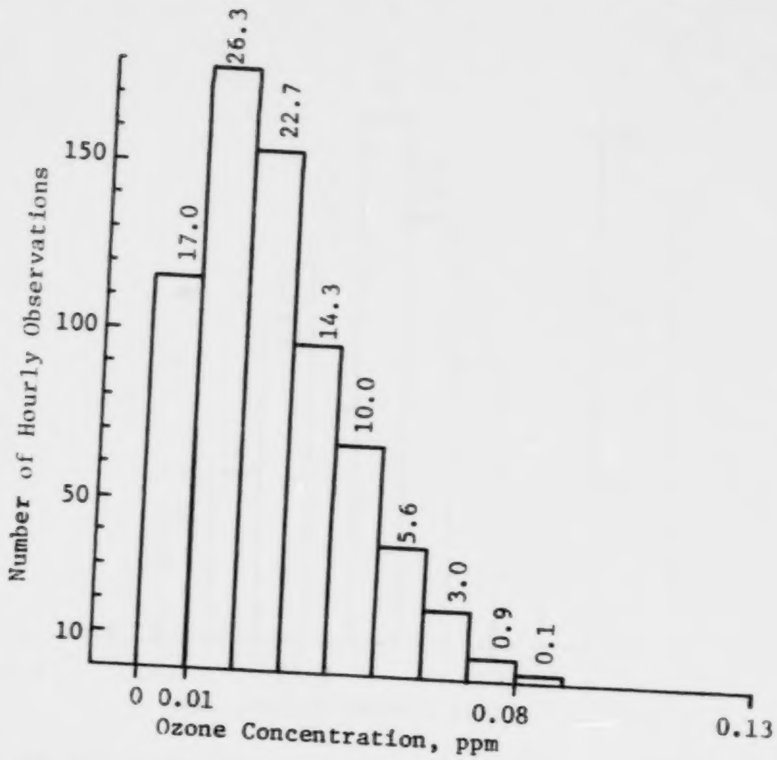

Figure 6.19. **Frequency distribution** of hourly ozone concentrations, **Tulsa Post Office.** September, 1977.

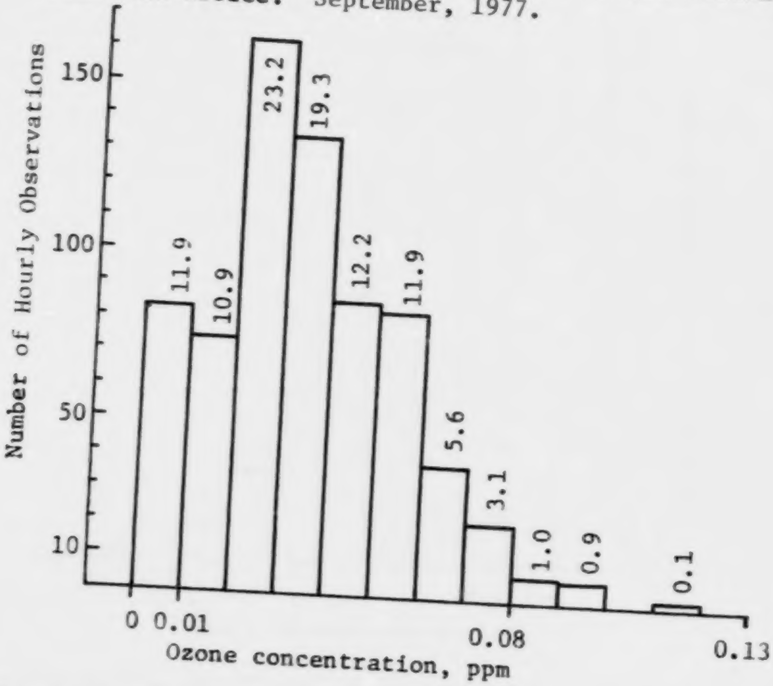

Figure 6.20. **Frequency distribution** of hourly ozone concentrations, **Sperry.** September, 1977.

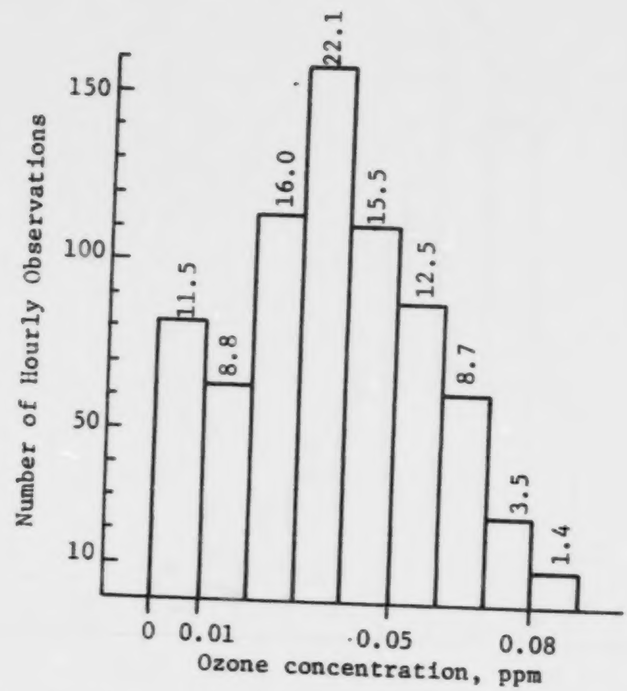

Figure 6.21. Frequency distribution of hourly ozone concentrations, Skiatook Lake. September, 1977.

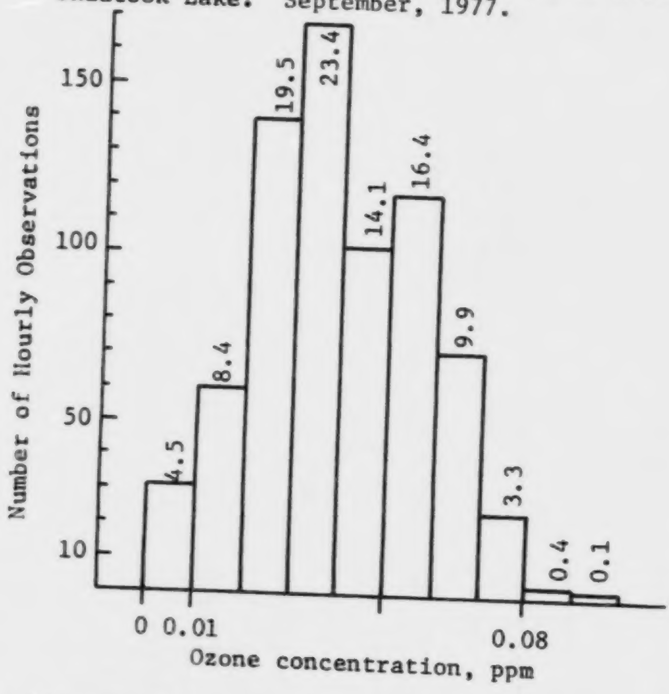

Figure 6.22. Frequency distribution of hourly ozone concentrations, Wynona. September, 1977.

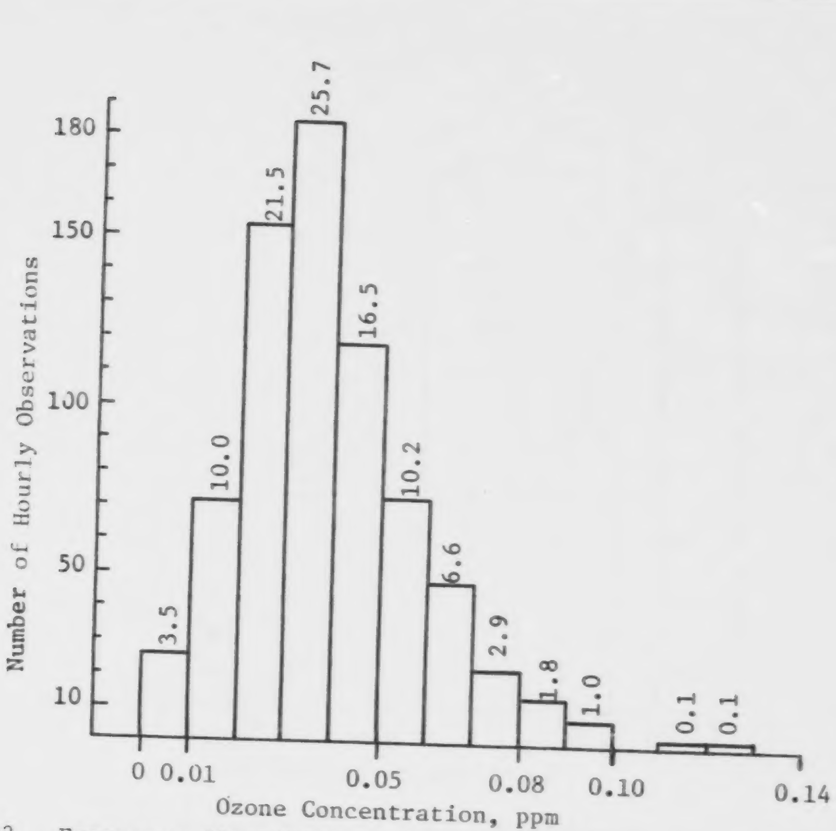

Figure 6.23. Frequency distribution of hourly ozone concentrations, Vera. September, 1977.

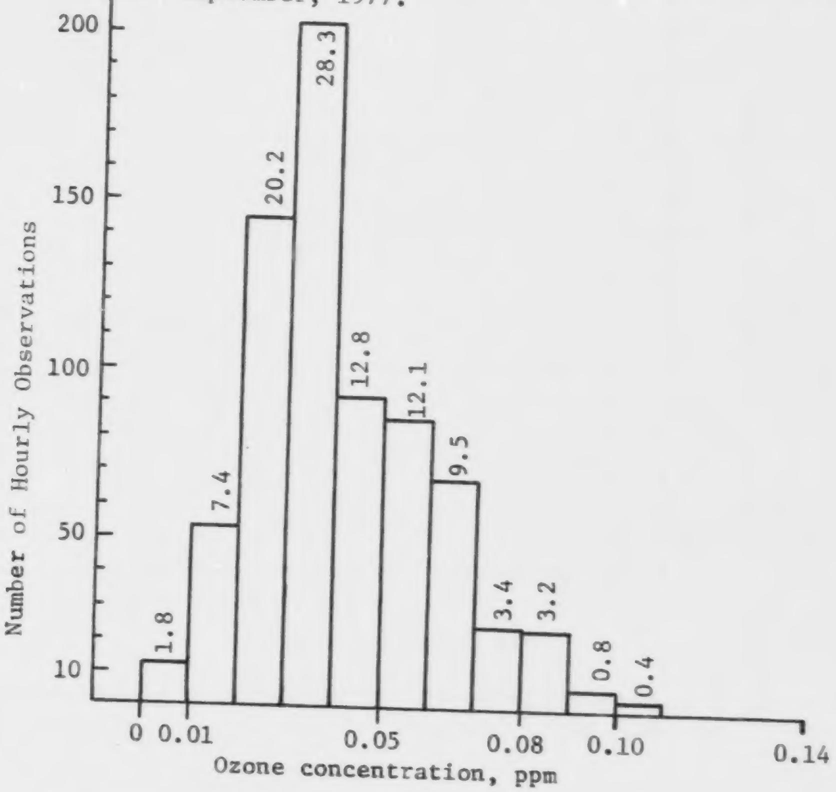

Figure 6.24 **Frequency** distribution of hourly ozone concentrations, **Ochelata.** September, 1977.

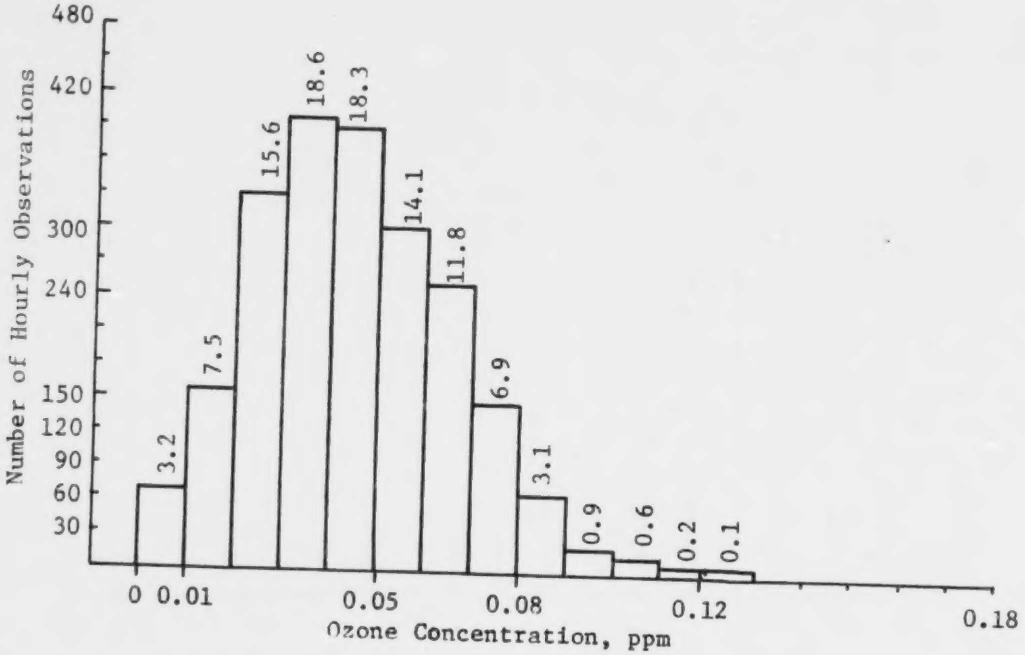

Figure 6.25. **Frequency distribution** of hourly ozone concentrations, **Liberty Mounds.** July, August, and September, 1977.

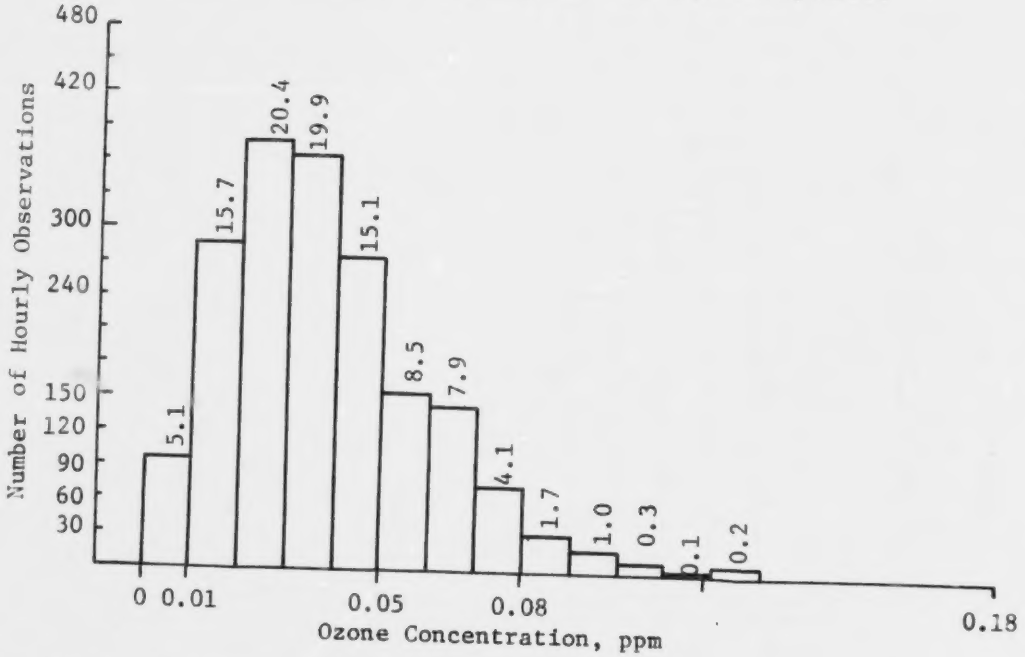

Figure 6.26. **Frequency distribution** of hourly ozone concentrations, **Tulsa City/County Health Department.** July, August, and September, 1977.

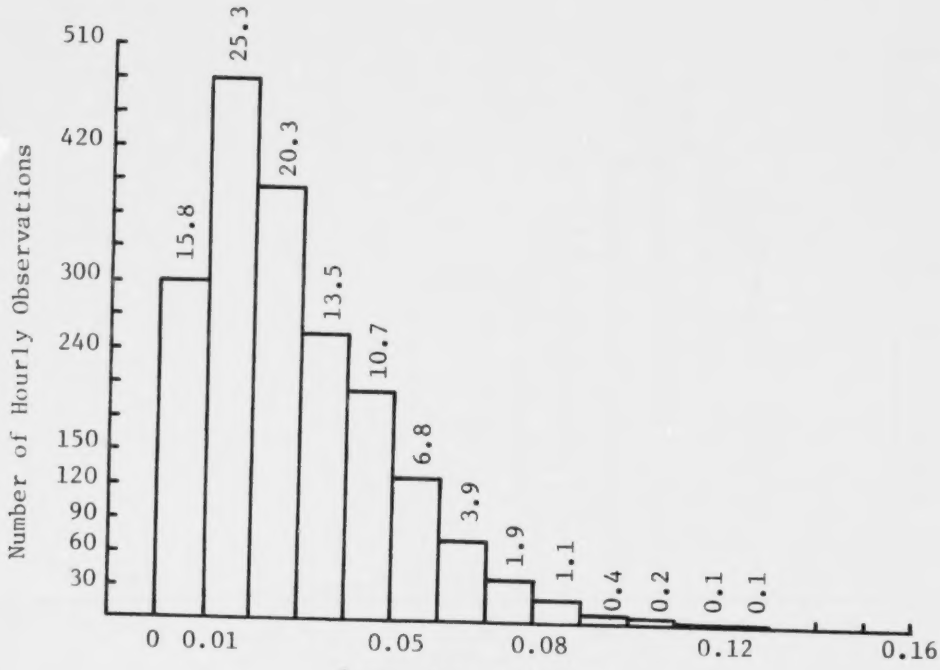

Figure 6.27. Frequency distribution of hourly ozone concentrations. Tulsa Post Office. July, August and September, 1977.

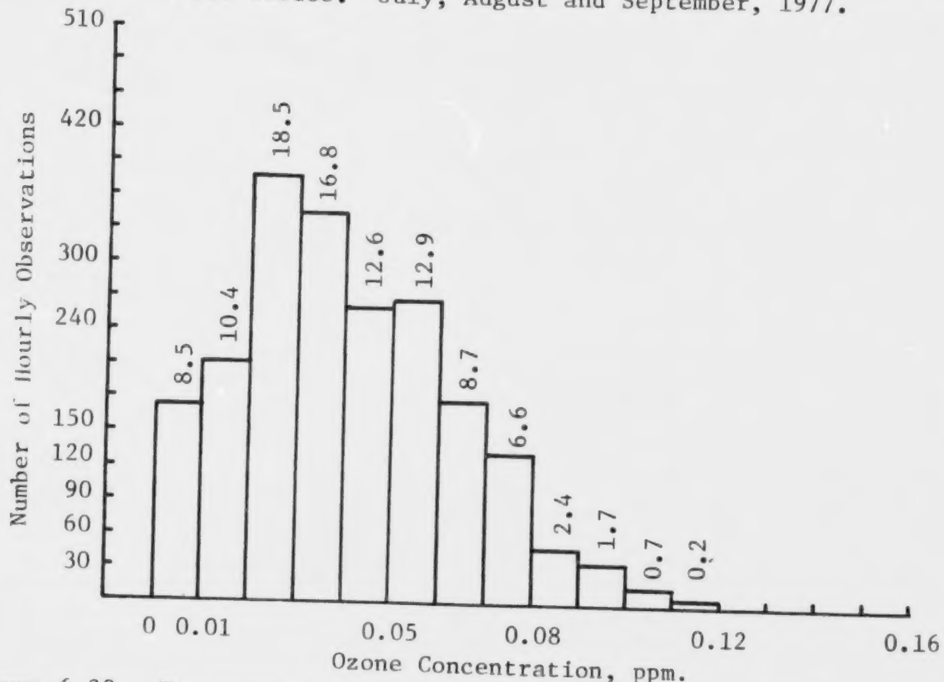

Figure 6.28. Frequency distribution of hourly ozone concentrations. Sperry. July, August and September, 1977.

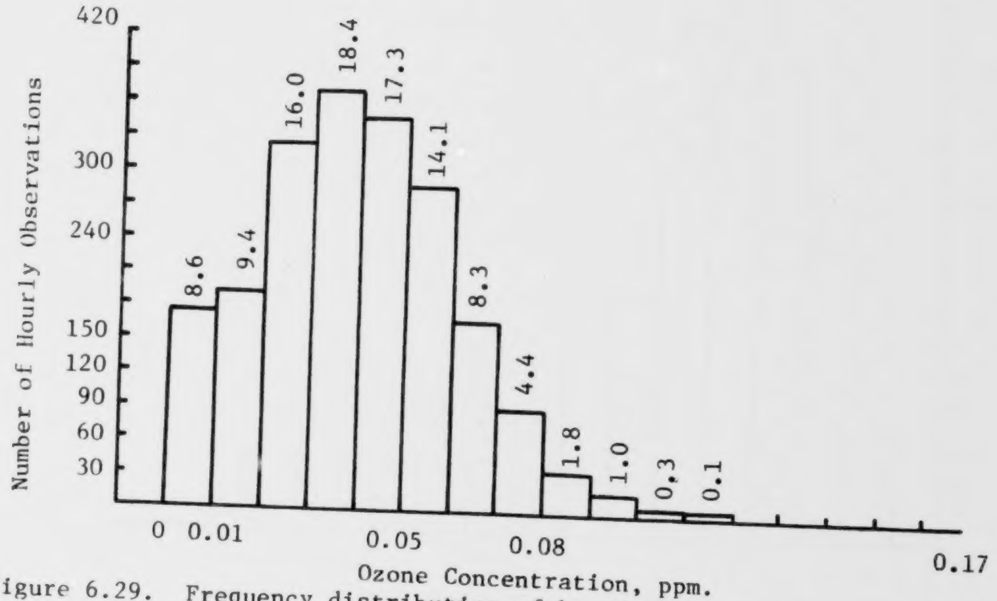

Figure 6.29. Frequency distribution of hourly ozone concentrations. Skiatook Lake. July, August and September, 1977.

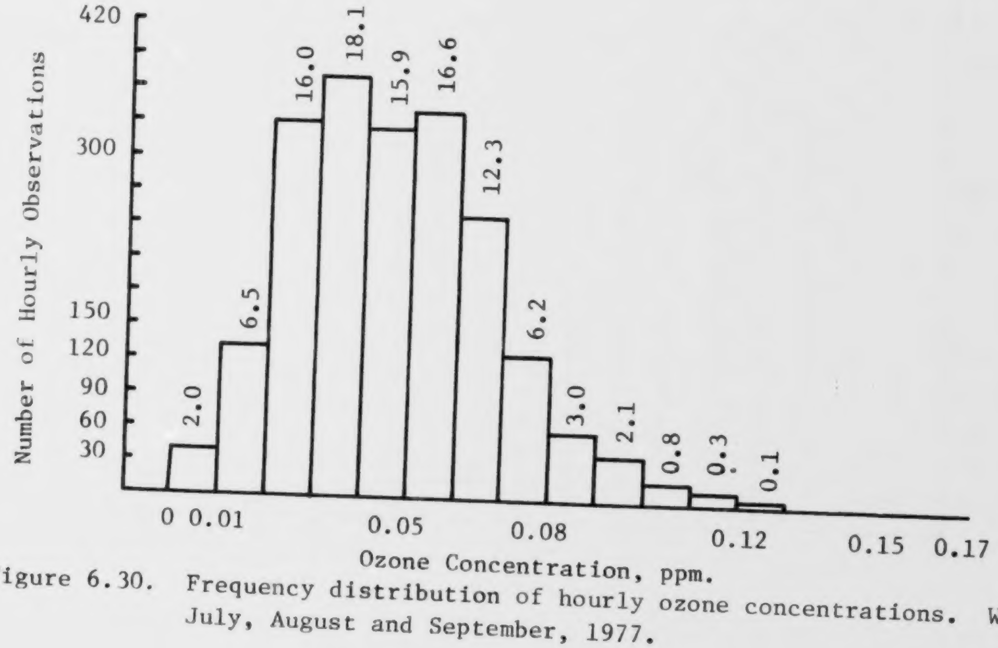

Figure 6.30. Frequency distribution of hourly ozone concentrations. Wynona. July, August and September, 1977.

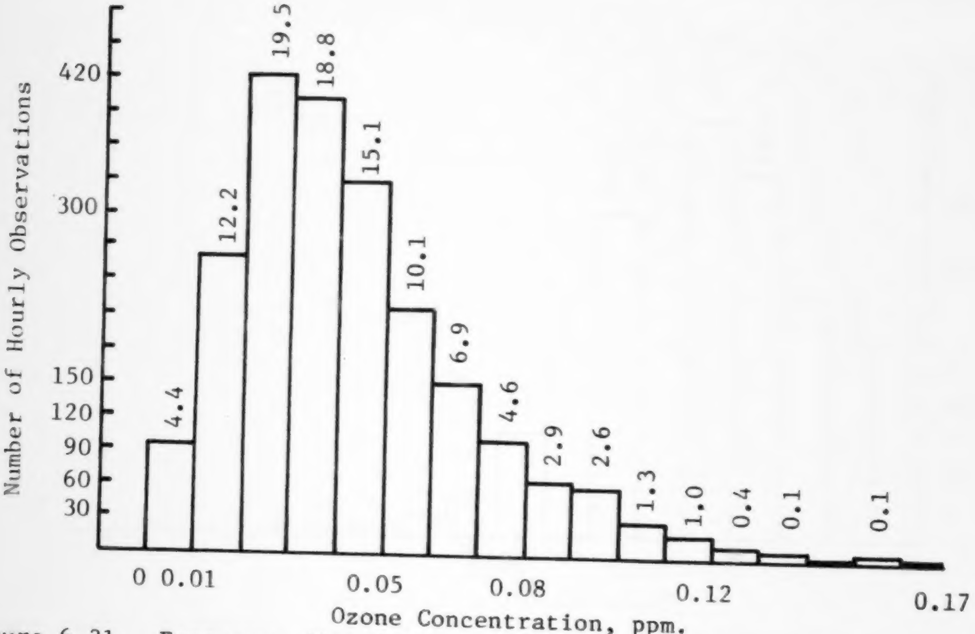

Figure 6.31. Frequency distribution of hourly ozone concentrations. Vera. July, August and September, 1977.

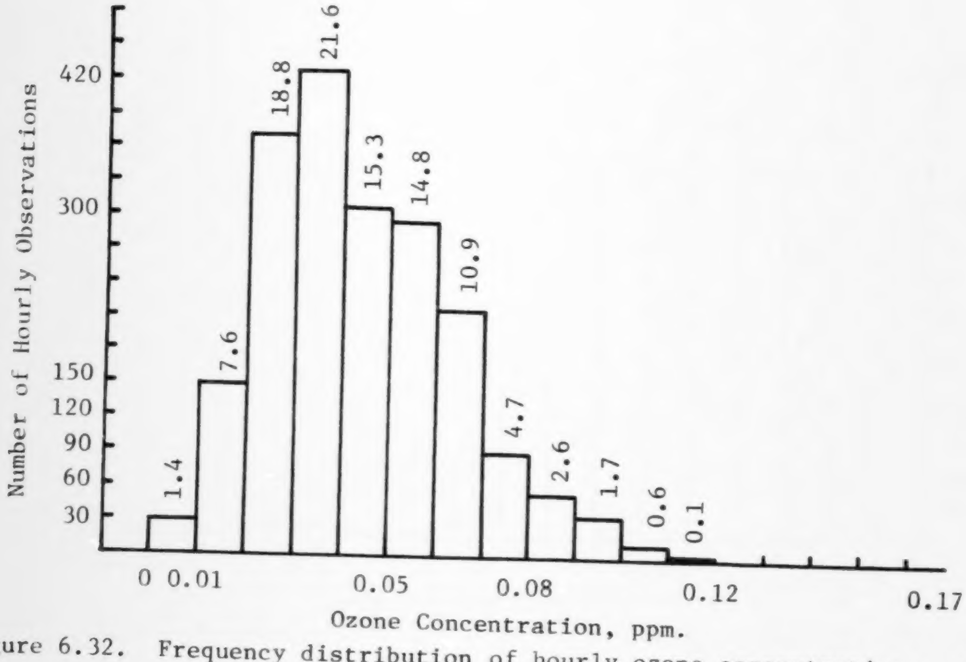

Figure 6.32. Frequency distribution of hourly ozone concentrations. Ochelata. July, August and September, 1977.

Table 6.14. Mean hourly standard deviations and number of values by hour of ozone for entire sampling period.

Hour, CST	Liberty Mounds		Tulsa Post Office		Tulsa City/County Health Department		Sperry	
	mean S_d	No. Values	mean S_d	No. Values	mean S_d	No. Values	mean S_d	No. Values
00	0.016	91	0.012	79	0.013	78	0.015	85
01	0.015	91	0.012	80	0.012	77	0.015	86
02	0.015	91	0.012	80	0.012	77	0.015	86
03	0.014	88	0.011	80	0.012	77	0.014	88
04	0.013	61	0.011	80	0.012	77	0.013	88
05	0.013	82	0.010	70	0.012	78	0.012	86
06	0.014	91	0.008	81	0.012	78	0.010	88
07	0.012	91	0.008	81	0.012	79	0.011	88
08	0.013	89	0.013	81	0.013	73	0.013	83
09	0.015	91	0.015	76	0.016	53	0.017	78
10	0.018	90	0.018	78	0.021	76	0.020	84
11	0.017	90	0.020	78	0.022	79	0.020	85
12	0.016	91	0.021	80	0.021	79	0.021	87
13	0.016	93	0.022	80	0.022	81	0.023	85
14	0.017	93	0.020	81	0.020	79	0.018	86
15	0.016	92	0.019	79	0.018	77	0.016	84
16	0.016	91	0.018	78	0.016	78	0.016	86
17	0.018	93	0.020	76	0.017	77	0.016	86
18	0.019	92	0.022	78	0.017	77	0.016	85
19	0.016	91	0.020	80	0.015	77	0.016	86
20	0.015	90	0.017	78	0.014	77	0.016	85
21	0.015	91	0.015	79	0.014	78	0.014	84
22	0.015	92	0.013	79	0.013	79	0.015	83
23	0.015	92	0.013	79	0.013	78	0.016	83

Table 6.14. Mean hourly standard deviations and number of values by hour of ozone for entire sampling period. (continued)

Hour, CST	Skiatook Lake		Vera		Wynona		Ochelata	
	mean S_d	No. Values	mean S_d	No. Values	mean S_d	No. Values	mean S_d	No. Values
00	0.017	87	0.013	92	0.016	86	0.012	84
01	0.017	83	0.013	92	0.016	86	0.012	80
02	0.017	87	0.012	91	0.015	84	0.012	84
03	0.017	85	0.012	87	0.014	88	0.012	85
04	0.015	85	0.012	92	0.014	88	0.011	84
05	0.014	83	0.011	92	0.013	88	0.010	83
06	0.014	85	0.011	87	0.013	88	0.010	85
07	0.012	83	0.010	92	0.012	87	0.010	85
08	0.012	83	0.011	87	0.014	81	0.012	71
09	0.012	82	0.013	78	0.014	86	0.013	80
10	0.015	83	0.020	90	0.016	86	0.015	86
11	0.015	84	0.022	90	0.018	85	0.016	81
12	0.016	84	0.024	92	0.018	85	0.016	81
13	0.018	83	0.025	92	0.018	85	0.017	85
14	0.017	85	0.025	93	0.017	87	0.018	86
15	0.016	83	0.022	91	0.017	86	0.017	84
16	0.016	78	0.019	91	0.018	87	0.016	83
17	0.015	83	0.019	85	0.019	86	0.015	79
18	0.017	84	0.018	89	0.018	88	0.014	82
19	0.016	86	0.016	92	0.017	88	0.013	84
20	0.016	88	0.014	92	0.016	87	0.013	84
21	0.016	86	0.013	92	0.016	88	0.011	85
22	0.017	88	0.012	93	0.016	88	0.012	84
23	0.018	88	0.012	92	0.016	87	0.012	84

Table 6.15. Summary of hourly ozone concentrations >0.08 ppm. July - September, 1977

	July			August			September			Three Month Period		
	Number Hours >0.08	Total Number Hours	Percent Hours >0.08	Number Hours >0.08	Total Number Hours	Percent Hours >0.08	Number Hours >0.08	Total Number Hours	Percent Hours >0.08	Number Hours >0.08	Total Number Hours	Percent Hours >0.08
Liberty Mounds	29	721	4.0	62	716	8.7	3	691	0.4	94	2128	4.4
Tulsa Post Office	19	474	4.0	10	739	1.4	1	677	0.1	30	1890	1.6
Tulsa City/County Health Department	25	524	4.8	25	698	3.6	8	617	1.3	58	1839	3.2
Sperry	44	597	7.4	42	740	5.7	11	699	1.6	97	2036	4.8
Skiatook Lake	10	592	1.7	40	660	6.1	6	714	0.8	56	1966	2.8
Vera	115	710	16.2	33	720	4.6	22	713	3.1	170	2143	7.9
Wynona	71	575	12.4	52	741	7.0	3	718	0.4	126	2034	6.2
Ochelata	34	561	6.1	31	704	4.4	28	713	3.9	93	1978	4.7

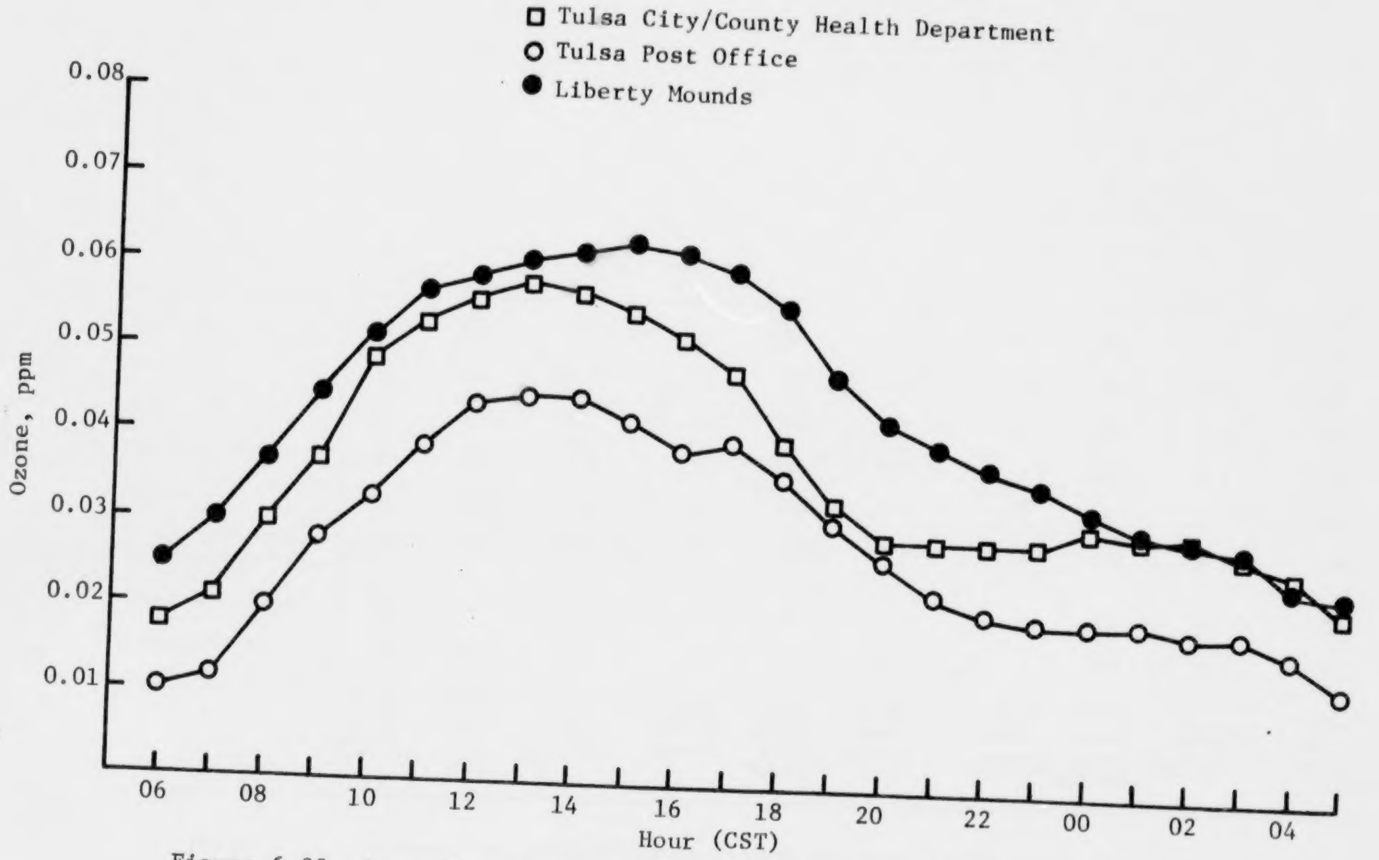

Figure 6.33. Mean diurnal ozone concentrations at Liberty Mounds, Tulsa City/County Health Department and Tulsa Post Office (July + August + September, 1977).

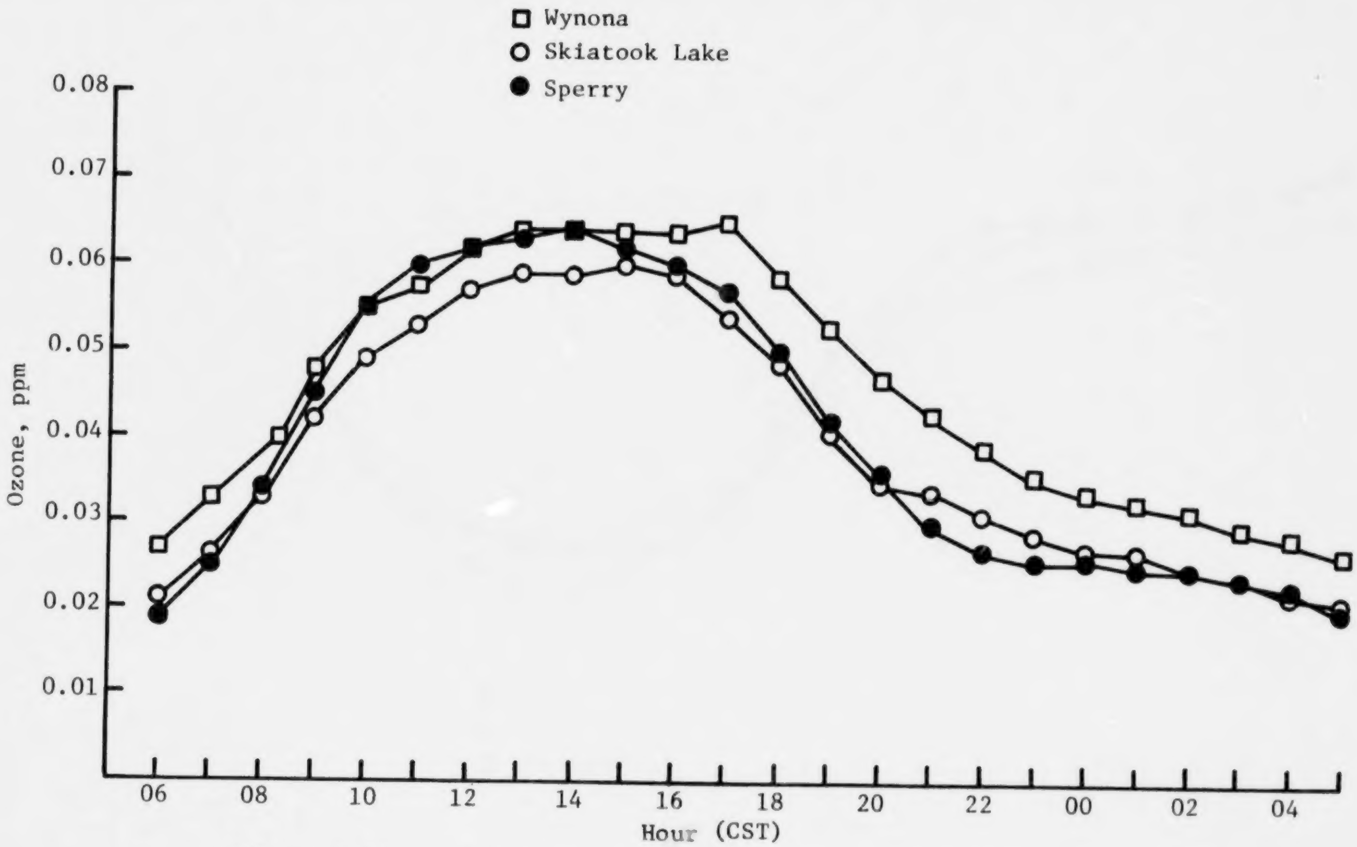

Figure 6.34. Mean diurnal ozone concentration at Sperry, Skiatook Lake, and Wynona (July + August + September, 1977).

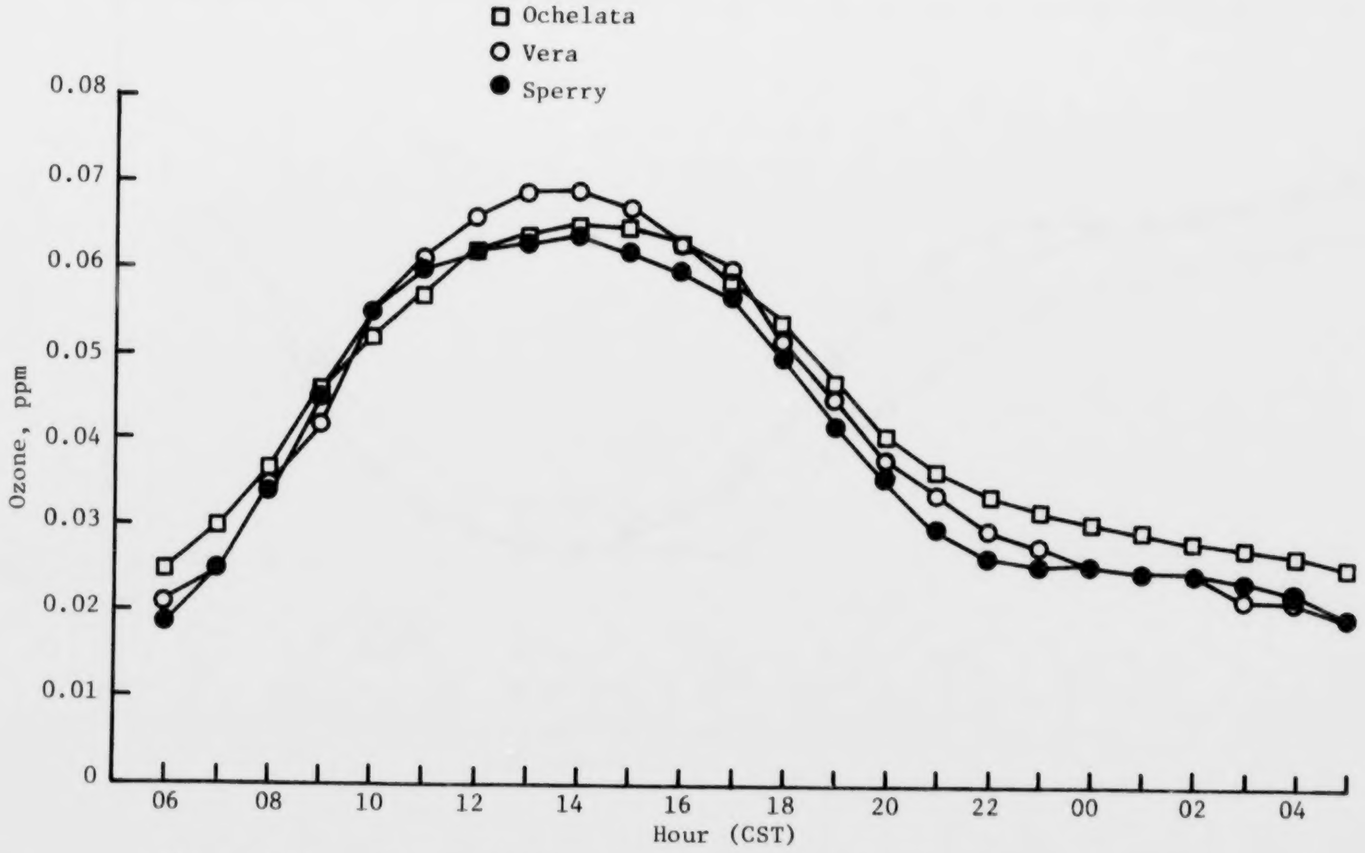

Figure 6.35. Mean diurnal ozone concentration at Sperry, Vera, and Ochelata (July + August + September, 1977).

6.3 OXIDES OF NITROGEN AND HYDROCARBON DATA SUMMARIES

6.3.1 Mean 0600 to 0900 CDT Concentrations of NO_x and NMHC

The 0600 to 0900 local time (CDT) is of interest to air pollution modelers and strategists. Average concentrations of NO_x (the sum of NO and NO_2) for this 3-hr period and the overall averages by month and for the total period were computed. The pollutant parameter NMHC (as measured by the Beckman air quality chromatograph and as measured by summing the concentrations of individual hydrocarbon species) was also calculated for the same time period. These values are shown in Table 6.16. The reader should note that the data for NO, NO_2, and NMHC (Beckman) tabulated in Volume II of the report are shown in central standard time (CST); the time frame 0600 to 0900 CDT corresponds to 0500 to 0800 CST.

6.3.2 Mean Hourly Standard Deviations for NO_2 and NMHC

Hourly means of nitrogen dioxide concentration and hourly standard deviations, and the number of values are listed in Table 6.17 for all sites. Average concentrations of NO_2 at sites south or north of Tulsa are at or near the minimum detectable limit for the analyzers used in this study. Table 6.18 lists the same information for NMHC as recorded by the continual Beckman 6800 chromatograph. NMHC concentrations were measured at the Wynona, Tulsa Post Office, and Tulsa Health Department sites.

6.3.3 Mean Daily 0600 to 0900 CDT NMHC/NO_x Ratios

Mean daily 0600 to 0900 CDT NMHC/NO_x ratios for the three sites where hydrocarbon species samples were collected and the three sites where NMHC was measured by automated chromatograph are given in Table 6.19. The median, maximum, and minimum ratios are also listed.

Values of NMHC/NO_x ratios (as determined using the automated chromatograph) are given for each day in Tables 6.20, 6.21, and 6.22 for the Post Office site, the Health Department site, and the Wynona site, respectively.

Values of NMHC/NO_x ratios (as determined by summing individual hydrocarbon species concentrations) are given in Tables 6.23, 6.24, and 6.25 for the Liberty Mounds, Tulsa Post Office, and Tulsa Health Department sites.

Table 6.16. Mean 0600 to 0900 CDT NO_x and NMHC concentrations by month and entire period

	July	August	September	Total period
		NO_x, ppm		
Liberty Mounds	0.009	0.006	0.005	0.007
Tulsa Post Office	0.065	0.073	0.055	0.065
Tulsa City/County Health Department	0.019	0.028	0.034	0.027
Sperry	0.016	0.016	0.020	0.017
Skiatook Lake	0.005	0.005	0.004	0.005
Vera	0.006	0.012	0.012	0.011
Wynona	0.006	0.006	0.004	0.005
Ochelata	0.011	0.007	0.005	0.007
		NMHC, ppmC (Beckman)		
Tulsa City/County Health Department	0.138	0.176	0.348	0.231
Tulsa Post Office	0.471	0.703	--	0.607
Wynona	--	0.230	0.571	0.530
		NMHC, ppmC (species summation)		
Liberty Mounds (less ethylene)	0.248	0.231	0.209	0.228
Tulsa Post Office	0.430	0.681	0.437	0.534
Tulsa City/County Health Department	0.257	0.407	0.268	0.317

Table 6.17. Hourly mean, $\overline{X}$, hourly standard deviation, σ, and number of hours for nitrogen dioxide, ppm

	Liberty Mounds			Tulsa Post Office			Tulsa City/County Health Department			Sperry		
Hour, CST	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values
00	0.004	0.005	88	0.025	0.013	76	0.011	0.010	84	0.009	0.006	85
01	0.004	0.005	88	0.024	0.013	76	0.009	0.008	84	0.008	0.006	85
02	0.004	0.004	88	0.023	0.014	75	0.007	0.006	84	0.007	0.006	84
03	0.004	0.004	86	0.021	0.011	75	0.007	0.007	84	0.007	0.004	84
04	0.003	0.004	65	0.020	0.011	66	0.008	0.007	85	0.007	0.004	84
05	0.005	0.005	88	0.025	0.010	77	0.012	0.008	83	0.009	0.005	85
06	0.006	0.005	90	0.029	0.010	79	0.019	0.010	81	0.011	0.005	85
07	0.005	0.004	90	0.032	0.012	79	0.020	0.011	80	0.011	0.006	84
08	0.004	0.003	84	0.031	0.012	72	0.017	0.011	77	0.010	0.007	83
09	0.004	0.004	87	0.031	0.013	78	0.013	0.009	55	0.009	0.007	73
10	0.004	0.004	88	0.031	0.014	77	0.012	0.007	77	0.008	0.006	81
11	0.004	0.004	88	0.030	0.015	78	0.011	0.006	81	0.007	0.003	85
12	0.004	0.004	90	0.026	0.013	78	0.011	0.006	82	0.006	0.003	83
13	0.003	0.003	88	0.026	0.013	79	0.010	0.006	82	0.006	0.003	86
14	0.004	0.004	88	0.027	0.015	78	0.011	0.006	84	0.006	0.003	85
15	0.003	0.003	89	0.029	0.016	77	0.012	0.007	82	0.006	0.002	85
16	0.003	0.003	89	0.029	0.016	77	0.014	0.008	81	0.007	0.003	85
17	0.003	0.003	89	0.029	0.017	76	0.015	0.009	81	0.008	0.003	84
18	0.004	0.004	88	0.028	0.016	76	0.019	0.010	82	0.009	0.004	85
19	0.005	0.004	88	0.028	0.015	77	0.023	0.013	82	0.011	0.006	83
20	0.005	0.004	89	0.028	0.013	77	0.024	0.014	83	0.012	0.007	83
21	0.005	0.005	89	0.029	0.013	77	0.021	0.013	81	0.013	0.008	84
22	0.005	0.005	90	0.028	0.013	76	0.017	0.012	83	0.012	0.008	84
23	0.004	0.004	90	0.025	0.012	77	0.014	0.011	83	0.010	0.007	84

Table 6.17. Hourly mean, $\overline{X}$, hourly standard deviation, σ, and number of hours for nitrogen dioxide, ppm (continued)

	Skiatook Lake			Vera			Wynona			Ochelata		
Hour, CST	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values
00	0.005	0.003	89	0.008	0.004	84	0.004	0.004	83	0.006	0.003	84
01	0.005	0.003	84	0.007	0.004	84	0.004	0.003	84	0.006	0.003	79
02	0.005	0.003	88	0.007	0.003	81	0.004	0.003	79	0.006	0.003	83
03	0.005	0.003	88	0.007	0.003	79	0.004	0.003	85	0.006	0.003	84
04	0.004	0.003	88	0.007	0.003	85	0.004	0.003	85	0.006	0.003	84
05	0.005	0.003	85	0.008	0.003	85	0.005	0.003	85	0.006	0.003	84
06	0.005	0.003	89	0.008	0.003	80	0.005	0.003	85	0.006	0.003	85
07	0.005	0.004	79	0.008	0.003	83	0.004	0.002	83	0.006	0.002	84
08	0.005	0.003	84	0.008	0.004	81	0.004	0.003	75	0.006	0.003	68
09	0.005	0.004	84	0.008	0.004	70	0.004	0.002	75	0.005	0.003	76
10	0.004	0.003	83	0.007	0.004	80	0.004	0.003	83	0.005	0.002	83
11	0.004	0.003	85	0.006	0.003	80	0.003	0.003	83	0.004	0.002	79
12	0.003	0.002	84	0.006	0.003	83	0.003	0.003	81	0.004	0.002	76
13	0.003	0.003	83	0.006	0.003	84	0.003	0.003	84	0.004	0.002	82
14	0.003	0.003	84	0.005	0.003	85	0.003	0.002	84	0.004	0.002	81
15	0.003	0.002	80	0.006	0.003	84	0.003	0.002	83	0.004	0.002	81
16	0.003	0.003	75	0.006	0.003	83	0.003	0.002	83	0.004	0.002	80
17	0.004	0.003	79	0.006	0.003	77	0.003	0.003	85	0.004	0.002	79
18	0.004	0.004	86	0.007	0.004	79	0.003	0.003	84	0.006	0.003	79
19	0.005	0.003	88	0.007	0.004	83	0.004	0.004	83	0.006	0.003	81
20	0.005	0.003	89	0.008	0.003	86	0.004	0.004	82	0.006	0.003	82
21	0.005	0.003	89	0.008	0.003	86	0.004	0.003	84	0.007	0.003	83
22	0.005	0.003	89	0.008	0.004	86	0.004	0.003	84	0.007	0.003	82
23	0.005	0.003	89	0.008	0.004	85	0.004	0.004	84	0.007	0.004	82

Table 6.18. Hourly mean, $\overline{X}$, hourly standard deviation, σ, and number of hours for nonmethane hydrocarbons, ppmC (Beckman 6800 data)

Hour, CST	Wynona			Tulsa Post Office			Tulsa City/County Health Department		
	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values	$\overline{X}$	σ	No. Values
00	0.434	0.415	26	0.302	0.204	39	0.127	0.159	51
01	0.405	0.291	26	0.337	0.283	39	0.121	0.164	50
02	0.460	0.404	26	0.345	0.359	39	0.129	0.233	48
03	0.483	0.427	26	0.373	0.338	38	0.132	0.201	48
04	0.490	0.435	25	0.460	0.371	22	0.151	0.223	48
05	0.593	0.572	25	0.562	0.766	39	0.154	0.171	50
06	0.589	0.626	25	0.625	0.442	41	0.249	0.340	50
07	0.398	0.346	26	0.639	0.378	41	0.286	0.297	52
08	0.225	0.082	26	0.579	0.429	41	0.210	0.226	50
09	0.227	0.086	26	0.545	0.412	43	0.160	0.166	45
10	0.195	0.059	25	0.427	0.203	43	0.154	0.221	42
11	0.189	0.063	26	0.436	0.250	42	0.128	0.162	49
12	0.194	0.086	21	0.378	0.192	42	0.137	0.129	51
13	0.173	0.068	23	0.462	0.382	42	0.126	0.123	53
14	0.165	0.072	23	0.504	0.522	41	0.152	0.136	52
15	0.156	0.060	23	0.422	0.272	41	0.174	0.139	50
16	0.147	0.050	24	0.353	0.165	39	0.224	0.212	50
17	0.175	0.067	24	0.323	0.267	40	0.271	0.393	50
18	0.230	0.098	24	0.309	0.185	41	0.337	0.338	50
19	0.352	0.359	24	0.397	0.510	41	0.370	0.323	51
20	0.351	0.283	24	0.334	0.215	41	0.367	0.439	51
21	0.351	0.208	23	0.354	0.245	40	0.300	0.392	52
22	0.438	0.470	24	0.403	0.498	39	0.181	0.214	52
23	0.411	0.359	26	0.326	0.239	39	0.175	0.317	50

Table 6.19. Mean daily 0600 to 0900 CDT NMHC/NO_x ratios with standard deviations, maximum, minimum, and median values

	Liberty Mounds ΣHC data[a]	Tulsa Post Office ΣHC data	Tulsa City/County Health Department ΣHC data	Tulsa Post Office Beckman 6800	Tulsa City/County Health Department Beckman 6800	Wynona Beckman 6800
July	7 cases	15 cases	15 cases	17 cases	3 cases	0 cases
Mean ratio value NMHC/NO_x	33.9	9.1	13.3	10.7	6.9	--
Standard deviation NMHC/NO_x ratio	32.4	4.5	6.2	5.1	3.5	--
Median value of NMHC/NO_x ratios	20.0	8.2	10.5	10.8	6.9	--
Maximum ratio value NMHC/NO_x	103.5	22.6	26.9	22.5	8.9	--
Minimum ratio value NMHC/NO_x	10.2	4.1	7.0	2.7	2.8	--
August	24 cases	28 cases	25 cases	23 cases	25 cases	0 cases
Mean ratio value NMHC/NO_x	47.2	13.6	20.7	13.2	7.9	--
Standard deviation NMHC/NO_x ratio	33.2	12.0	23.5	8.7	5.9	--
Median value of NMHC/NO_x ratios	35.5	11.4	12.8	12.8	6.1	--
Maximum ratio value NMHC/NO_x	125.0	64.5	121.4	31.0	24.7	--
Minimum ratio value NMHC/NO_x	11.8	1.8	6.9	1.7	0.9	--

See footnote at end of table.

(continued)

Table 6.19 (continued)

	Liberty Mounds ΣHC data[a]	Tulsa Post Office ΣHC data	Tulsa City/County Health Department ΣHC data	Tulsa Post Office Beckman 6800	Tulsa City/County Health Department Beckman 6800	Wynona Beckman 6800
September	22 cases	27 cases	27 cases	0 cases	16 cases	18 cases
Mean ratio value $NMHC/NO_x$	46.2	9.2	9.3	--	10.2	155.2
Standard deviation $NMHC/NO_x$ ratios	30.1	3.3	5.8	--	5.4	85.9
Median value of $NMHC/NO_x$ ratios	35.9	9.2	7.1	--	9.0	153.3
Maximum ratio value $NMHC/NO_x$	120.0	16.2	33.0	--	26.7	352.0
Minimum ratio value $NMHC/NO_x$	8.1	2.6	4.0	--	1.3	47.5
Total Period	53 cases	70 cases	67 cases	40 cases	44 cases	19 cases
Mean ratio value $NMHC/NO_x$	45.0	10.9	14.4	12.1	8.7	169.1
Standard deviation $NMHC/NO_x$ ratio	31.5	8.3	15.7	7.4	5.7	99.9
Median value of $NMHC/NO_x$ ratios	34.4	9.5	10.5	11.4	8.4	159.2
Maximum ratio value $NMHC/NO_x$	125.0	64.5	121.4	31.0	26.7	380.0
Minimum ratio value $NMHC/NO_x$	8.1	1.8	4.0	1.7	0.9	47.5

[a] Less ethylene.

Table 6.20. Daily 0600-0900 CDT average NMHC (Beckman 6800 gas chromatograph) and NO_x, and ratio of NMHC to NO_x. Tulsa Post Office

Date	NMHC ppmC	Average 6-9 CDT NO_x,ppm	$\frac{NMHC}{NO_x}$	Date	NMHC ppmC	Average 6-9 CDT NO_x,ppm	$\frac{NMHC}{NO_x}$
7/15	0.570	0.053	10.8	8/06	0.250	0.149	1.7
16	0.520	0.047	11.1	07	0.380	0.209	1.8
17	0.130	0.027	4.8	08	0.600	0.192	3.1
18	0.650	0.045	14.4	09	0.690	0.137	5.0
19	0.580	0.051	11.4	10	0.810	—	—
20	0.560	0.038	14.7	11	0.470	0.030	15.7
21	0.360	0.073	4.9	12	0.320	0.025	12.8
22	0.340	0.027	12.6	13	0.350	0.042	8.3
23	0.620	0.036	17.2	14	0.330	0.012	27.5
24	0.350	0.128	2.7	15	0.940	0.074	12.7
25	0.870	0.090	9.7	16	—	0.102	—
26	0.530	0.040	13.3	17	—	0.027	—
27	0.280	0.026	10.8	18	0.740	0.052	14.2
28	0.360	0.016	22.5	19	0.710	0.047	15.1
29	0.540	0.068	7.9	20	0.530	0.037	14.3
30	0.540	0.150	3.6	21	0.830	0.029	28.6
31	0.200	0.023	8.7	22	3.110	0.128	24.3
8/01	0.980	0.088	11.1	23	0.720	0.033	21.8
02	1.110	0.075	14.8	24	0.470	0.036	13.1
03	0.900	0.071	12.7	25	0.620	0.020	31.0
04	0.380	0.071	5.4	26	0.430	0.056	7.7
05	—	0.068	—	27	0.200	0.116	1.7

Table 6.21. Daily 0600-0900 CDT average NMHC (Beckman 6800 gas chromatograph) and NO_x, and ratio of NMHC to NO_x. Tulsa City/County Health Department

Date	NMHC ppmC	Average 6-9 CDT NO_x,ppm	$\frac{NMHC}{NO_x}$
7/25	0.050	0.018	2.8
26	—	0.029	—
27	—	0.041	—
28	0.160	0.018	8.9
29	0.340	0.038	8.9
30	0.0	0.018	—
31	—	0.026	—
8/01	—	0.078	—
02	0.800	0.055	14.5
03	0.080	0.028	2.9
04	0.620	0.047	13.2
05	0.240	0.026	9.2
06	0.150	0.010	15.0
07	0.050	0.005	10.0
08	0.170	0.010	17.0
09	0.130	0.014	9.3
10	0.220	0.018	12.2
11	0.270	0.027	10.0
12	0.060	—	—
13	0.010	0.011	0.9
14	0.010	0.009	1.1
15	0.190	0.037	5.1
16	0.040	0.011	3.6
17	0.150	0.024	6.3
18	0.360	0.061	5.9
19	0.110	0.036	3.1
20	0.100	0.025	4.0
21	0.060	0.018	3.3
22	0.790	0.032	24.7
23	—	0.026	—
24	0.070	0.038	1.8
25	0.0	0.012	—
8/26	0.030	0.014	2.1
27	0.0	0.005	—
28	0.0	0.003	—
29	0.070	0.026	2.7
30	0.190	0.025	7.6
31	0.130	0.011	11.8
9/01	0.260	0.040	6.5
02	0.420	0.055	7.6
03	0.320	0.040	8.0
04	0.120	0.009	13.3
05	0.110	0.012	9.2
06	0.420	0.039	10.8
07	0.450	0.050	9.0
08	0.780	0.073	10.7
09	0.430	0.027	15.9
10	0.260	0.026	10.0
11	0.160	0.006	26.7
12	0.210	0.024	8.75
13	—	0.021	—
14	—	0.017	—
15	—	0.030	—
16	0.650	0.098	6.6
17	0.010	0.008	1.3
18	0.0	0.014	—
19	0.120	0.011	10.9
20	1.190	0.149	8.0

Table 6.22. Daily 0600-0900 CDT average NMHC (Beckman 6800 gas chromatograph) and NO_x, and ratio of NMHC to NO_x. Wynona

Date	NMHC ppmC	Average 6-9 CDT NO_x,ppm	$\frac{NMHC}{NO_x}$
8/29	0.140	0.0	—
30	0.380	0.001	380.0
31	0.170	0.0	—
9/01	0.120	0.0	—
02	1.060	0.004	265.0
03	1.630	0.006	271.7
04	1.340	0.008	167.5
05	0.150	0.0	—
06	0.370	0.003	123.3
07	0.680	0.003	226.7
08	1.760	0.005	352.0
09	0.900	0.005	180.0
10	0.190	0.004	47.5
9/11	0.290	0.006	48.3
12	0.150	0.0	—
13	0.330	0.002	165.0
14	0.140	0.002	70.0
15	0.260	0.005	52.0
16	0.460	0.003	153.3
17	0.150	0.0	—
18	0.200	0.003	66.7
19	—	0.0	—
20	1.340	0.007	191.4
21	0.260	0.002	130.0
22	0.410	0.004	102.5
23	0.360	0.002	180.0

Table 6.23. 0600-0900 CDT average NMHC (sum of individual hydrocarbon species less ethylene) and NO_x, and ratio of NMHC to NO_x. Liberty Mounds

Date	ΣNMHC ppmC	Average 6-9 CDT NO_x, ppm	$\frac{\Sigma \text{NMHC}}{NO_x}$	Date	ΣNMHC ppmC	Average 6-9 CDT NO_x, ppm	$\frac{\Sigma \text{NMHC}}{NO_x}$
7/14	--	0.019	--	8/22	1.042	0.021	49.6
15	--	0.011	--	23	0.136	0.003	45.3
16	--	0.011	--	24	0.215	0.000	--
17	--	0.008	--	25	0.125	0.001	125.0
18	--	0.014	--	26	0.125	0.002	62.5
19	0.144	0.014	10.2	27	0.052	0.003	17.3
20	0.117	0.008	14.6	28	0.088	0.002	44.0
21	0.240	0.012	20.0	29	0.065	0.002	32.5
22	0.536	0.018	29.8	30	0.103	0.005	20.6
23	0.327	0.008	40.9	31	0.154	0.002	77.0
24	--	0.007	--	9/01	0.314	0.000	--
25	--	0.007	--	02	0.303	0.010	30.3
26	--	0.005	--	03	0.620	0.018	34.4
27	--	0.010	--	04	--	--	--
28	--	0.005	--	05	0.044	0.002	22.0
29	--	0.015	--	06	0.528	0.008	66.0
30	0.162	0.009	18.0	07	0.229	0.007	32.7
31	0.207	0.002	103.5	08	0.596	0.020	29.8
8/01	--	--	--	09	0.160	0.009	17.8
02	0.424	0.012	35.3	10	0.065	0.008	8.1
03	0.209	0.017	12.3	11	0.120	0.001	120.0
04	0.097	0.008	12.1	12	0.106	0.002	53.0
05	--	0.004	--	13	0.095	0.002	47.5
06	--	--	--	14	0.129	0.000	--
07	0.077	0.003	25.7	15	0.081	0.000	--
08	0.323	0.007	46.1	16	0.171	0.006	28.5
09	0.223	0.006	31.2	17	0.125	0.003	41.7
10	0.216	0.015	14.4	18	0.068	0.003	22.7
11	0.226	0.007	32.3	19	0.149	0.014	10.6
12	0.130	0.011	11.8	20	0.455	0.015	30.3
13	0.181	0.006	30.2	21	0.225	0.003	75.0
14	--	0.005	--	22	0.204	0.002	102.0
15	0.343	0.003	114.3	23	--	0.003	--
16	--	--	--	24	0.159	0.000	--
17	0.214	0.006	35.7	25	0.121	0.003	40.3
18	0.225	0.002	112.5	26	0.279	0.003	93.0
19	0.233	0.003	77.7	27	0.148	0.002	74.0
20	--	0.005	--	28	0.083	0.000	--
21	0.541	0.008	67.6	29	0.075	0.002	37.5
				30	--	0.002	--

Table 6.24. 0600-0900 CDT average NMHC (sum of individual hydrocarbon species) and NO_x, and ratio of NMHC to NO_x. Tulsa Post Office

Date	ΣNMHC ppmC	Average 6-9 CDT NO_x,ppm	$\frac{\Sigma NMHC}{NO_x}$
7/14	0.531	0.077	6.9
15	0.392	0.053	7.4
16	0.331	0.047	7.0
17	--	0.027	--
18	--	0.045	--
19	--	0.051	--
20	0.310	0.038	8.2
21	0.327	0.073	4.5
22	0.298	0.027	11.0
23	0.421	0.036	11.7
24	0.528	0.128	4.1
25	0.687	0.090	7.6
26	0.364	0.040	9.1
27	0.288	0.026	11.1
28	0.362	0.016	22.6
29	0.567	0.068	8.3
30	0.771	0.150	5.1
31	0.274	0.023	11.9
8/01	0.794	0.088	9.0
02	0.857	0.075	11.4
03	0.852	0.071	12.0
04	0.528	0.071	7.4
05	--	0.068	--
06	--	0.149	--
07	0.531	0.209	2.5
08	0.719	0.192	3.7
09	0.487	0.137	3.6
10	0.584	--	--
11	0.448	0.030	14.9
12	0.435	0.025	17.4
13	0.332	0.042	7.9
14	0.774	0.012	64.5
15	1.065	0.074	14.4
16	1.161	0.102	11.4
17	0.404	0.027	15.0
18	0.535	0.052	10.3
19	0.507	0.047	10.8
20	0.536	0.037	14.5
21	0.767	0.029	26.4
8/22	3.684	0.128	28.7
23	0.478	0.033	14.5
24	0.592	0.036	16.4
25	0.431	0.020	21.6
26	0.565	0.056	10.1
27	0.204	0.116	1.8
28	0.224	0.108	2.1
29	0.367	0.032	11.5
30	0.329	0.029	11.3
31	0.571	0.105	5.4
9/01	0.348	0.037	9.4
02	0.640	0.063	10.2
03	0.367	0.031	11.8
04	0.175	0.018	9.7
05	0.131	0.012	10.9
06	0.519	0.037	14.0
07	0.493	0.059	8.4
08	0.819	0.085	9.6
09	0.808	--	--
10	0.187	0.025	7.5
11	0.150	0.011	13.6
12	0.348	0.054	6.4
13	0.462	0.054	8.6
14	0.154	0.020	7.7
15	0.358	0.057	6.3
16	0.870	0.095	9.2
17	0.225	0.085	2.6
18	--	0.136	--
19	0.282	0.038	7.4
20	1.298	0.203	6.4
21	0.289	0.071	4.1
22	0.508	0.035	14.5
23	0.393	0.089	4.4
24	0.172	0.021	8.2
25	0.390	0.030	13.0
26	0.653	0.082	8.0
27	0.300	0.032	9.4
28	0.278	0.025	11.1
29	0.614	0.038	16.2
30	--	--	--

Table 6.25. 0600-0900 CDT average NMHC (sum of individual hydrocarbon species) and NO$_x$, and ratio of NMHC to NO$_x$. Tulsa City/County Health Department

Date	ΣNMHC ppmC	Average 6-9 CDT NO$_x$,ppm	ΣNMHC / NO$_x$	Date	ΣNMHC ppmC	Average 6-9 CDT NO$_x$,ppm	ΣNMHC / NO$_x$
7/14	0.234	0.029	8.1	8/22	1.127	0.132	8.5
15	0.242	0.013	18.6	23	–	0.026	–
16	–	0.012	–	24	0.425	0.038	11.2
17	0.215	0.008	26.9	25	1.457	0.012	121.4
18	–	0.026	–	26	0.389	0.014	27.8
19	0.279	–	–	27	0.163	0.005	32.6
20	0.294	0.012	24.5	28	–	0.003	–
21	0.239	0.019	12.6	29	0.332	0.026	12.8
22	0.251	0.031	8.1	30	0.222	0.025	8.9
23	0.335	0.032	10.5	31	0.136	0.011	12.4
24	0.176	0.009	19.6	9/01	0.217	0.040	5.4
25	0.270	0.018	15.0	02	0.393	0.055	7.1
26	0.242	0.029	8.3	03	0.285	0.040	7.1
27	0.289	0.041	7.0	04	–	0.009	–
28	0.173	0.018	9.6	05	0.140	0.012	11.7
29	0.397	0.038	10.4	06	0.194	0.039	5.0
30	0.179	0.018	9.9	07	0.288	0.050	5.8
31	0.289	0.026	11.1	08	0.519	0.073	7.1
8/01	0.537	0.078	6.9	09	0.290	0.027	10.7
02	0.559	0.055	10.2	10	0.103	0.026	4.0
03	0.343	0.028	12.2	11	–	0.006	–
04	0.396	0.047	8.4	12	0.163	0.024	6.8
05	0.223	0.026	8.6	13	0.255	0.021	12.1
06	–	0.010	–	14	0.117	0.017	6.9
07	0.270	0.005	54.0	15	0.283	0.030	9.4
08	–	0.010	–	16	0.566	0.098	5.8
09	0.193	0.014	13.8	17	0.105	0.008	13.1
10	0.477	0.018	26.5	18	0.069	0.014	4.9
11	0.330	0.027	12.2	19	0.154	0.011	14.0
12	–	–	–	20	0.885	0.149	5.9
13	0.158	0.011	14.4	21	0.166	0.019	8.7
14	0.141	0.009	15.7	22	0.274	0.034	8.1
15	0.421	0.037	11.4	23	0.205	0.014	14.6
16	0.281	0.011	25.5	24	0.228	0.022	10.4
17	0.309	0.024	12.9	25	0.165	0.005	33.0
18	0.444	0.061	7.3	26	0.516	0.078	6.6
19	–	0.036	–	27	0.100	0.016	6.2
20	0.368	0.025	14.7	28	0.122	0.025	4.9
21	0.476	0.018	26.4	29	0.447	0.029	15.4
				30	–	–	–

6.3.4 Diurnal Plots of Mean Hourly THC, CH_4 and NMHC Values

Mean diurnal patterns for total hydrocarbon measurements are shown in Figure 6.36. Similar patterns for methane and nonmethane hydrocarbons are shown in Figures 6.37 and 6.38.

6.4 METEOROLOGICAL DATA SUMMARIES

6.4.1 Tabulated Frequency of Wind Directions

Table 6.26 shows the tabulated case count and percentage of time the wind direction is from successive 10° compass increments for the four sites that monitored this parameter. The case count of calms (expressed as 0° for wind speeds less than 1 mph) is also listed.

Tables 6.27, 6.28, 6.29, and 6.30 give similar information for 30° increments of wind direction for the entire 3-month period.

6.4.2 Tabulated Frequency of Wind Speed

Hourly frequencies of wind speed for the 3-month period are given in Tables 6.31, 6.32, 6.33, and 6.34. The increments of wind speed values (in miles per hour) include a 0.0 to 0.9-mph range (i.e., calm periods) and successive 5-mph increments

6.4.3 Precipitation and Maximum Temperatures

Daily maximum temperatures (°F) and 24-hr total precipitation (inches water) for Tulsa are illustrated for the months of July, August, and September 1977 in Figures 6.39, 6.40, and 6.41.

6.5 INDIVIDUAL HYDROCARBON SPECIES DATA SUMMARY

Hydrocarbon samples were primarily collected at three site, Liberty Mounds, Tulsa Health Department and Tulsa Post Office, during the 0600 to 0900 CDT period. Additional collections were made at other sites during the period of airborne sampling. Table 3.3 summarizes the number of samples taken at each site as well as the number of samples successfully analyzed for all species sought. Explanations of unsuccessful analyses are listed in Volume II with the data printouts.

Average values, ppbC, for the 0600 to 0900 CDT time frame collection for three sites are given in Table 6.35 for alkanes and Table 6.36 for alkene, alkyne, and aromatic compounds.

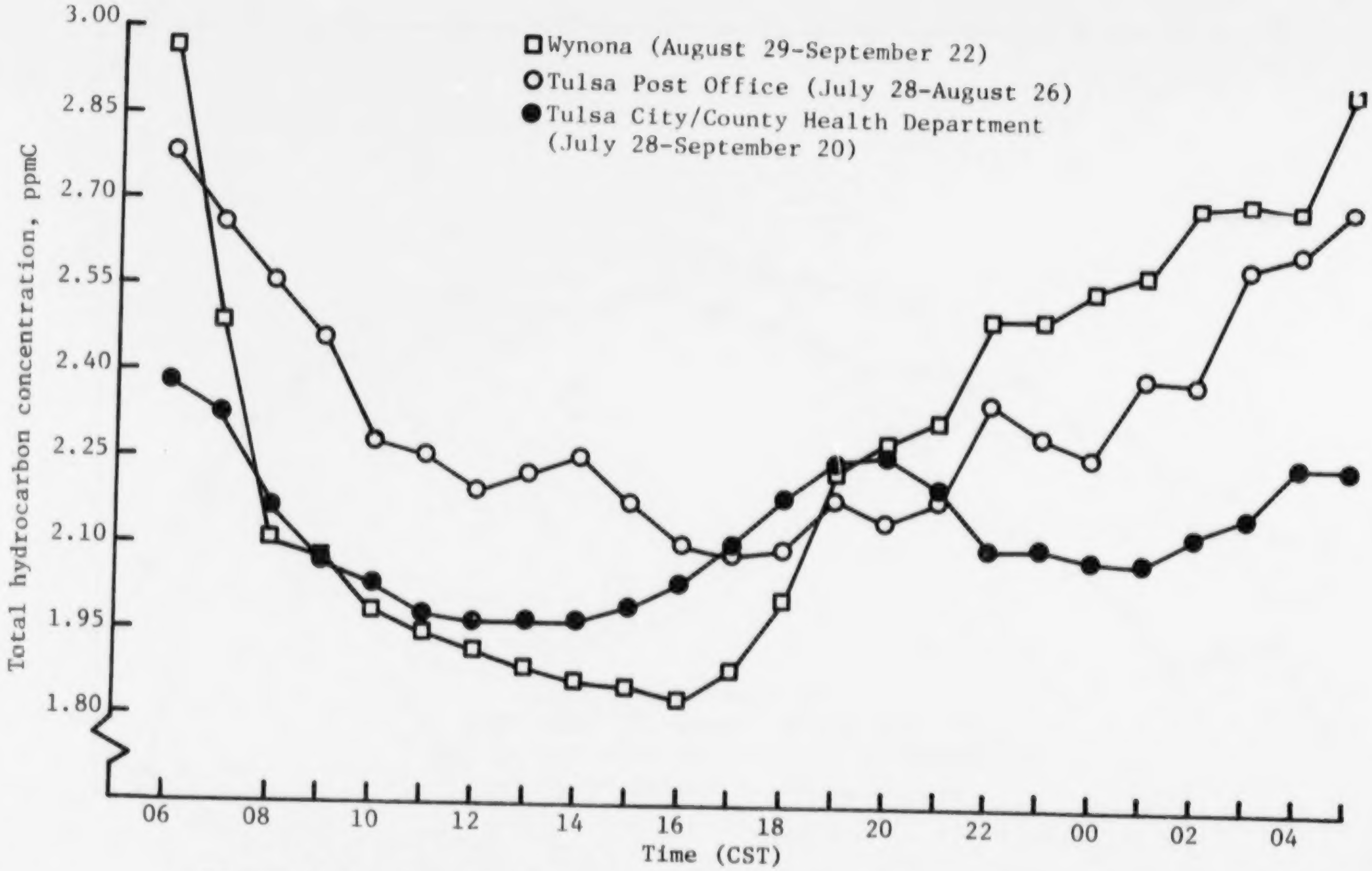

Figure 6.36. Mean diurnal concentrations of total hydrocarbons at Wynona, Tulsa Post Office, and Tulsa City/County Health Department

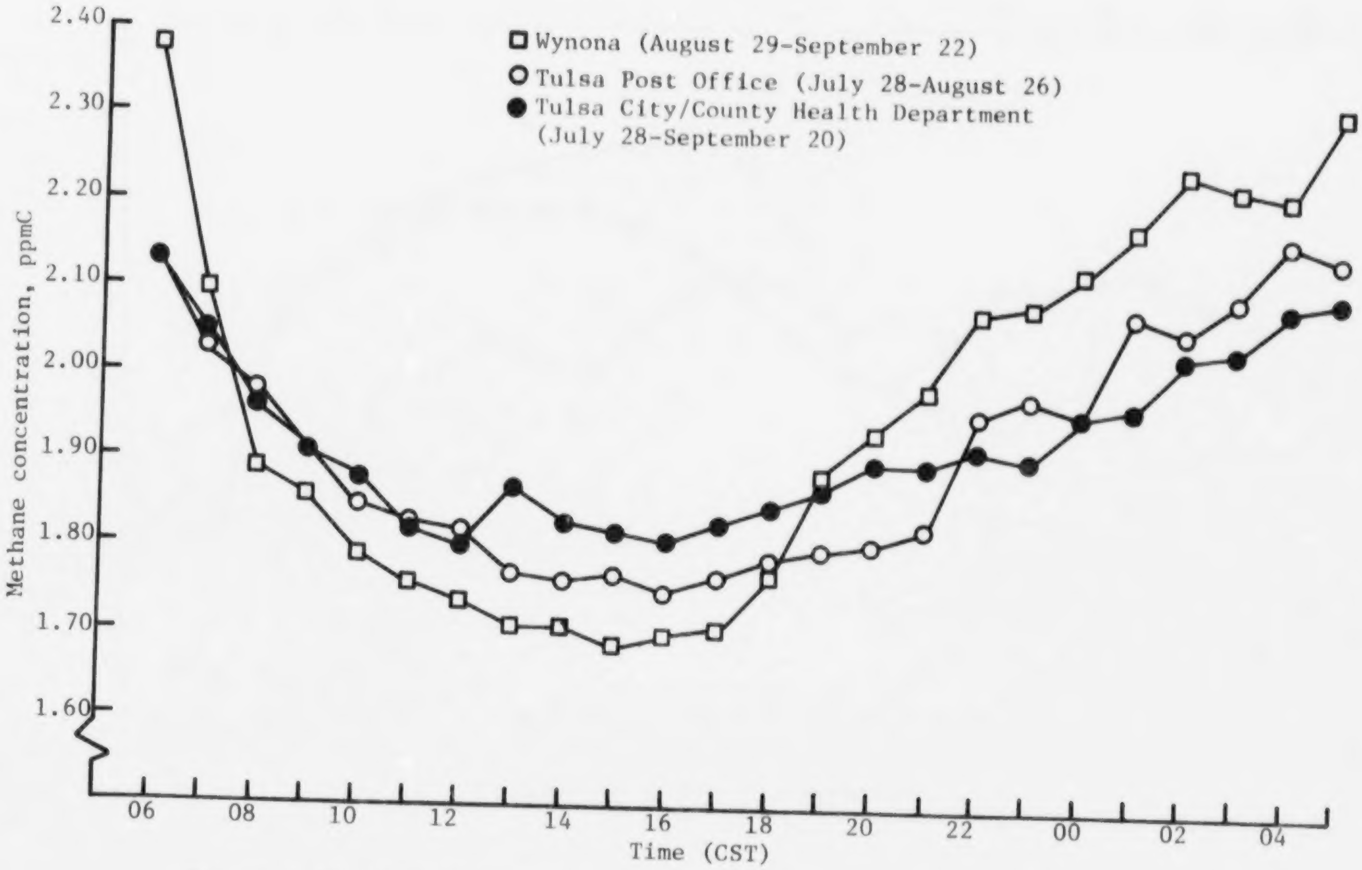

Figure 6.37. Mean diurnal concentrations of methane at Wynona, Tulsa Post Office, and Tulsa City/County Health Department

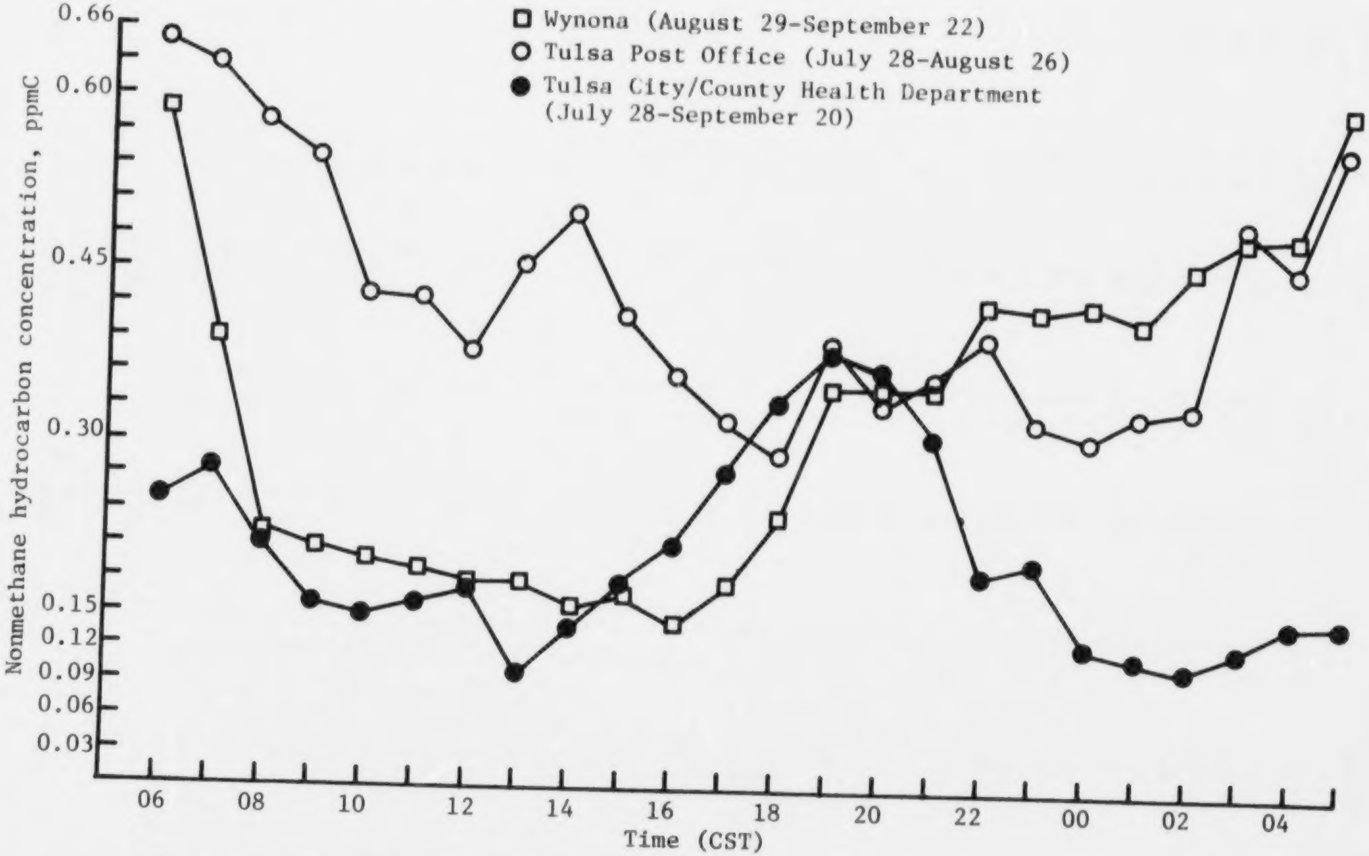

Figure 6.38. Mean diurnal concentration of nonmethane hydrocarbons at Wynona, Tulsa Post Office, and Tulsa City/County Health Department

Table 6.26. Wind direction; tabulation frequency by 10° of direction increment for entire study period

Degree range	Liberty Mounds		Health Department		Wynona		Ochelata	
	Cases	%	Cases	%	Cases	%	Cases	%
0 (calm)	131	6.6	4	0.2	84	4.2	236	11.4
10	41	2.2	16	0.8	89	4.6	42	2.3
20	51	2.7	18	0.9	69	3.6	81	4.4
30	52	2.8	37	1.8	79	4.1	76	4.1
40	47	2.5	68	3.3	39	2.0	65	3.5
50	48	2.6	48	2.3	55	2.9	57	3.1
60	55	3.0	50	2.4	62	3.2	18	1.0
70	52	2.8	16	0.8	30	1.6	28	1.5
80	29	1.6	22	1.1	25	1.3	32	1.7
90	46	2.5	68	3.3	44	2.3	24	1.3
100	30	1.6	30	1.4	36	1.9	24	1.3
110	19	1.0	10	0.5	40	2.1	20	1.1
120	33	1.8	20	1.0	28	1.5	10	0.5
130	23	1.2	83	4.0	30	1.6	17	0.9
140	32	1.7	51	2.4	66	3.4	26	1.4
150	80	4.3	50	2.4	81	4.2	22	1.2
160	73	3.9	101	4.8	163	8.5	36	2.0
170	101	5.4	137	6.6	198	10.3	57	3.1
180	277	14.9	587	28.0	275	14.3	128	7.0
190	123	6.6	205	9.8	99	5.2	343	18.6
200	105	5.6	126	6.0	110	5.7	387	21.0
210	179	9.6	54	2.6	27	1.4	94	5.1
220	72	3.9	49	2.3	18	0.9	28	1.5
230	58	3.1	15	0.7	20	1.0	15	0.8
240	57	3.1	10	0.5	23	1.2	15	0.8
250	23	1.2	9	0.4	11	0.6	6	0.3
260	10	0.5	8	0.4	7	0.4	14	0.8
270	30	1.6	31	1.5	17	0.9	10	0.5
280	9	0.5	3	0.1	5	0.3	11	0.6
290	5	0.3	5	0.2	8	0.4	7	0.4
300	17	0.9	1	0	17	0.9	12	0.7
310	6	0.3	25	1.2	5	0.3	11	0.6
320	10	0.5	5	0.2	9	0.5	18	1.0
330	12	0.6	1	0	22	1.1	21	1.1
340	17	0.9	2	0.1	39	2.0	21	1.1
350	15	0.8	4	0.2	66	3.4	25	1.4
360	24	1.3	126	6.0	6	0.3	30	1.6
TOTAL CASES	1992		2095		2002		2067	
TOTAL MINUS CALMS	1861		2091		1918		1831	

Table 6.27. Hourly frequencies of calms and wind direction by 30° increments for July-September, 1977. Liberty Mounds

Hour CST	Cases		Calms		10-30°		40-60°		70-90°		100-120°		130-150°		160-180°		190-210°		220-240°		250-270°		280-300°		300-330°		340-360°	
	All	Less Calms	No.	% All Cases	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
00	83	73	10	12.0	6	8.2	7	9.6	3	4.1	1	1.4	6	8.2	25	34.2	16	21.9	3	4.1	1	1.4	0	0.0	1	1.4	4	5.5
01	83	71	12	14.5	9	12.7	3	4.2	3	4.2	1	1.4	6	8.4	19	26.8	21	29.6	2	2.8	4	5.6	0	0.0	1	1.4	2	2.8
02	83	69	14	16.9	6	8.7	6	8.7	2	2.9	3	4.3	4	5.8	21	30.4	14	20.1	8	11.6	2	2.9	0	0.0	2	2.9	1	1.4
03	83	72	11	13.2	8	11.1	3	4.2	3	4.2	4	5.6	5	6.9	17	23.6	15	20.8	11	15.3	2	2.8	2	2.8	2	2.8	0	0.0
04	83	76	7	8.4	10	13.2	5	6.6	5	6.6	3	3.9	4	5.3	15	19.7	11	14.5	14	18.4	1	1.3	5	6.6	2	2.6	1	1.3
05	83	71	12	14.5	8	11.3	1	1.4	7	9.9	2	2.8	5	7.0	16	22.5	11	15.5	9	12.7	5	7.0	1	1.4	1	1.4	5	7.0
06	83	71	12	14.5	7	9.9	4	5.6	5	7.0	2	2.8	5	7.0	14	19.7	14	19.7	7	9.9	3	4.2	4	5.6	3	4.2	3	4.2
07	83	71	12	14.5	8	11.3	6	8.4	4	5.6	7	9.9	4	5.6	14	19.7	13	18.3	7	9.9	2	2.8	2	2.8	2	2.8	2	2.8
08	82	72	11	13.4	8	11.1	5	6.9	5	6.9	2	2.8	5	6.9	17	23.6	18	25.0	7	9.7	1	1.4	1	1.4	1	1.4	1	1.4
09	83	79	4	4.8	6	7.6	9	11.4	4	5.1	8	10.1	5	6.3	12	15.2	16	20.3	14	17.7	1	1.3	1	1.3	0	0.0	3	3.8
10	82	80	2	2.4	6	7.5	10	12.5	7	8.7	4	5.0	7	8.7	12	15.0	17	21.2	13	16.2	2	2.5	1	1.2	1	1.2	0	0.0
11	82	80	2	2.4	4	5.0	6	7.5	9	11.2	0	0.0	11	13.7	14	17.5	22	27.5	9	11.2	3	3.7	1	1.2	0	0.0	1	1.2
12	82	80	2	2.4	3	3.7	7	8.7	3	3.7	4	5.0	6	7.5	16	20.0	23	28.7	10	12.5	5	6.2	0	0.0	0	0.0	3	3.7
13	84	83	1	1.2	3	3.6	8	9.6	1	1.2	4	4.8	5	6.0	15	18.1	25	25.0	12	14.4	4	4.8	1	1.2	1	1.2	4	4.8
14	84	83	1	1.2	2	2.4	6	7.2	5	6.0	3	3.6	5	6.0	13	15.7	28	33.7	8	9.6	6	7.2	2	2.4	2	2.4	3	3.6
15	84	82	2	2.4	5	6.1	3	3.7	8	9.8	0	0.0	7	8.5	17	20.7	25	30.5	10	12.2	2	2.4	2	2.4	0	0.0	3	3.7
16	84	83	1	1.2	3	3.6	8	9.6	4	4.8	4	4.8	3	3.6	22	2.4	19	22.9	9	10.8	5	6.0	2	2.4	0	0.0	4	4.8
17	83	83	0	0.0	6	7.2	5	6.0	9	10.8	6	7.2	3	3.6	21	25.3	21	25.3	6	7.2	3	3.6	2	2.4	0	0.0	1	1.2
18	84	84	0	0.0	5	5.9	5	5.9	11	13.1	5	5.9	4	4.8	24	28.6	16	19.0	6	7.1	2	2.4	1	1.2	2	2.4	2	2.4
19	83	83	0	0.0	5	6.0	6	7.2	11	13.3	2	2.4	8	9.6	28	33.7	13	15.7	4	4.8	0	0.0	2	2.4	2	2.4	2	2.4
20	83	83	0	0.0	5	6.0	10	12.0	6	7.2	6	7.2	6	7.2	26	31.3	12	14.5	6	7.2	1	1.2	1	1.2	2	2.4	2	2.4
21	83	81	2	2.4	8	9.9	7	8.6	5	6.2	2	2.5	10	12.3	26	32.1	11	13.6	5	6.2	3	3.7	0	0.0	1	1.2	3	3.7
22	83	77	6	7.2	7	9.1	10	12.9	5	6.5	3	3.9	5	6.5	24	31.2	13	16.9	3	3.9	4	5.2	0	0.0	1	1.3	2	2.6
23	83	76	7	8.4	6	7.9	10	13.2	2	2.6	5	6.6	7	9.2	23	30.3	13	17.1	4	5.3	1	1.3	0	0.0	1	1.3	4	5.3

Table 6.28. Hourly frequencies of calms and wind direction by 30° increments for Tulsa City/ County Public Health Department. July-September, 1977

Hour CST	Cases		Calms		10-30°		40-60°		70-90°		100-120°		130-150°		160-180°		190-210°		220-240°		250-270°		280-300°		300-330°		340-360°	
	All	Less Calms	No.	% All Cases	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
00	87	87	0	0.0	0	0.0	10	11.5	1	1.1	4	4.6	10	11.5	28	32.2	24	27.6	3	3.4	1	1.1	0	0.0	1	1.1	5	5.7
01	87	87	0	0.0	2	2.3	6	6.9	4	4.6	4	4.6	8	9.2	27	31.0	25	28.7	3	3.4	1	1.1	1	1.1	2	2.3	4	4.6
02	87	86	1	1.1	1	1.2	7	8.1	4	4.7	4	4.7	8	9.3	22	25.6	28	32.6	5	5.8	1	1.2	0	0.0	2	2.3	4	4.7
03	87	87	0	0.0	1	1.1	4	4.6	5	5.7	3	3.4	12	13.8	21	24.1	25	28.7	8	9.2	0	0.0	1	1.1	2	2.3	5	5.7
04	87	87	0	0.0	5	5.7	2	2.3	3	3.4	3	3.4	8	9.2	24	27.6	31	35.6	3	3.4	2	2.3	0	0.0	2	2.3	4	4.6
05	87	87	0	0.0	2	2.3	8	9.2	3	3.4	2	2.3	6	6.9	26	29.9	28	32.2	3	3.4	2	2.3	1	1.1	1	1.1	5	5.7
06	86	86	0	0.0	5	5.8	9	10.5	4	4.7	2	2.3	10	11.6	20	23.3	29	33.7	4	4.7	1	1.2	0	0.0	2	2.3	0	0.0
07	86	86	0	0.0	4	4.7	7	8.1	4	4.7	0	0.0	10	11.6	18	20.9	29	33.7	5	5.8	0	0.0	0	0.0	1	1.2	8	9.3
08	87	87	0	0.0	4	4.6	6	6.9	5	5.7	6	6.9	8	9.2	17	19.5	31	35.6	4	4.6	1	1.1	1	1.1	0	0.0	4	4.6
09	88	88	0	0.0	2	2.3	10	11.4	2	2.3	2	2.3	9	10.2	14	15.9	29	33.0	14	15.9	2	2.3	1	1.1	0	0.0	3	3.4
10	88	88	0	0.0	2	2.3	10	11.4	6	6.8	1	1.1	5	5.7	10	11.4	32	36.4	14	15.9	5	5.7	0	0.0	0	0.0	3	3.4
11	89	89	0	0.0	2	2.2	8	9.0	4	4.5	2	2.2	6	6.7	9	10.1	29	32.6	15	16.9	9	10.1	0	0.0	1	1.1	4	4.5
12	89	89	0	0.0	1	1.1	8	9.0	3	3.4	4	4.5	3	3.4	19	21.3	26	29.2	13	14.6	5	5.6	1	1.1	2	2.2	4	4.5
13	89	89	0	0.0	1	1.1	9	10.1	3	3.4	4	4.5	2	2.2	22	24.7	28	31.5	8	9.0	1	1.1	2	2.2	4	4.5	5	5.6
14	90	90	0	0.0	1	1.1	9	10.0	4	4.4	4	4.4	3	3.3	28	31.1	22	24.4	6	6.7	4	4.4	1	1.1	1	1.1	7	7.8
15	90	90	0	0.0	2	2.2	9	10.0	2	2.2	4	4.4	5	5.6	26	28.9	26	28.9	5	5.6	2	2.2	0	0.0	2	2.2	7	7.8
16	88	88	0	0.0	2	2.3	7	8.0	2	2.3	1	1.1	12	13.6	20	22.7	26	29.5	3	3.4	1	1.1	1	1.1	2	2.3	11	12.5
17	87	87	0	0.0	0	0.0	8	9.2	4	4.6	3	3.4	12	13.8	21	24.1	23	26.4	1	1.1	2	2.3	0	0.0	2	2.3	11	12.6
18	87	87	0	0.0	0	0.0	11	12.6	4	4.6	0	0.0	11	12.6	26	29.9	20	23.0	2	2.3	1	1.1	1	1.1	2	2.3	9	10.3
19	86	86	0	0.0	0	0.0	12	14.0	2	2.3	0	0.0	13	15.1	31	36.0	17	19.8	2	2.3	2	2.3	0	0.0	1	1.2	6	7.0
20	85	85	0	0.0	0	0.0	13	15.3	3	3.5	0	0.0	15	17.6	31	36.5	15	17.6	2	2.4	0	0.0	0	0.0	1	1.2	5	5.9
21	86	86	0	0.0	0	0.0	12	14.0	5	5.8	0	0.0	10	11.6	36	41.9	14	16.3	2	2.3	1	1.2	0	0.0	0	0.0	6	7.0
22	86	86	0	0.0	0	0.0	8	9.3	7	8.1	3	3.5	7	8.1	35	40.7	16	18.6	2	2.3	1	1.2	0	0.0	0	0.0	7	8.1
23	86	86	0	0.0	0	0.0	9	10.5	4	4.7	3	3.5	10	11.6	32	37.2	21	24.4	1	1.2	0	0.0	0	0.0	1	1.2	5	5.8

Table 6.29. Hourly frequencies of calms and wind direction by 30° increments for Wynona. July-September, 1977

Hour CST	Cases		Calms		10-30°		40-60°		70-90°		100-120°		130-150°		160-180°		190-210°		220-240°		250-270°		280-300°		300-330°		340-360°	
	All	Less Calms	No.	% All Cases	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
00	84	81	3	3.6	12	14.8	4	4.9	3	3.7	4	4.9	3	3.7	31	38.3	10	12.3	3	3.7	2	2.5	0	0.0	5	6.2	4	4.9
01	84	80	4	4.8	12	15.0	7	8.8	3	3.8	3	3.8	1	1.3	28	35.0	12	15.0	2	2.5	1	1.3	2	2.5	3	3.8	6	7.5
02	84	77	7	8.3	10	13.0	3	3.9	2	2.6	3	3.9	1	1.3	28	36.4	14	18.2	3	3.9	1	1.3	1	1.3	3	3.9	8	10.4
03	84	78	6	7.1	11	14.1	2	2.6	4	5.1	4	5.1	5	6.4	25	32.1	12	15.4	2	2.6	1	1.3	1	1.3	3	3.8	8	10.3
04	84	79	5	6.0	10	12.7	7	8.9	1	1.3	4	5.1	4	5.1	29	36.7	12	15.2	0	0.0	0	0.0	2	2.5	1	1.3	9	11.4
05	84	79	5	6.0	12	15.2	5	6.3	6	7.6	3	3.8	6	7.6	25	31.6	9	11.4	2	2.5	0	0.0	0	0.0	2	2.5	9	11.4
06	84	80	4	4.8	13	16.3	9	11.3	6	7.5	4	4.8	5	6.3	27	33.8	6	7.5	1	1.3	0	0.0	2	2.5	2	2.5	5	6.3
07	83	79	4	4.8	13	16.5	5	6.3	6	7.6	3	3.8	5	6.3	26	32.9	12	15.2	1	1.3	2	2.5	4	4.8	1	1.3	1	1.3
08	83	80	3	3.6	10	12.5	9	11.3	2	2.5	6	7.5	4	5.0	23	28.8	16	20.0	1	1.3	3	3.6	5	6.3	1	1.3	0	0.0
09	81	80	1	1.2	11	13.8	8	10.0	4	5.0	3	3.6	5	6.3	18	22.5	15	18.8	10	12.5	2	2.5	2	2.5	0	0.0	2	2.5
10	81	81	0	0.0	9	11.1	10	12.3	2	2.5	5	6.2	3	3.7	29	23.5	18	22.2	6	7.4	2	2.5	2	2.5	3	3.7	2	2.5
11	82	80	2	2.4	8	10.0	9	11.3	1	1.3	3	3.6	3	3.6	25	31.3	18	22.5	7	8.8	1	1.3	1	1.3	0	0.0	4	5.0
12	83	83	0	0.0	4	4.8	11	13.3	3	3.6	2	2.4	5	6.0	24	28.9	19	22.9	4	4.8	5	6.0	1	1.2	2	2.4	3	3.6
13	83	81	2	2.4	6	7.4	6	7.4	7	8.6	2	2.5	5	6.2	25	30.9	15	18.5	5	7/2	4	4.9	1	1.2	1	1.2	4	4.9
14	83	81	2	2.4	7	8.6	7	8.6	6	7.4	3	3.7	9	11.1	29	35.8	8	9.9	4	4.9	3	3.7	0	0.0	0	0.0	5	6.2
15	83	78	5	6.0	5	6.4	5	6.4	7	9.0	3	3.8	7	9.0	36	46.2	4	5.1	2	2.6	3	3.8	3	3.8	0	0.0	3	3.8
16	84	83	1	1.2	7	8.4	7	8.4	7	8.4	3	3.6	12	14.5	30	36.1	5	6.0	2	2.4	1	1.2	0	0.0	4	4.8	5	6.0
17	84	80	4	4.8	9	11.3	9	11.3	5	6.3	7	8.8	13	16.3	26	32.5	4	5.0	1	1.3	2	2.5	0	0.0	0	0.0	4	5.0
18	84	81	3	3.6	11	13.6	5	6.2	6	7.4	10	12.3	16	19.8	25	30.9	3	3.7	2	2.5	0	0.0	0	0.0	1	1.2	2	2.5
19	84	81	3	3.6	8	9.9	7	8.6	6	7.4	8	9.9	16	19.8	25	30.9	2	2.5	1	1.2	1	1.2	2	2.5	0	0.0	5	6.2
20	84	80	4	4.8	10	12.5	9	11.3	2	s.5	10	12.5	16	20.0	23	28.8	4	5.0	0	0.0	1	1.3	0	0.0	1	1.3	4	5.0
21	84	79	5	6.0	12	15.2	5	6.3	4	5.1	3	3.8	15	19.0	27	34.2	5	6.3	0	0.0	0	0.0	0	0.0	1	1.3	7	8.9
22	84	79	5	6.0	13	16.5	4	5.1	4	5.1	4	5.1	11	13.9	30	38.0	5	6.3	2	2.5	0	0.0	0	0.0	1	1.3	5	6.3
23	84	78	6	7.1	14	17.9	3	3.8	2	2.6	4	5.1	7	9.0	32	41.0	8	10.3	0	0.0	0	0.0	1	1.3	1	1.3	6	7.7

Table 6.30. Hourly frequencies of calms and wind direction by 30° increments for Ochelata. July - September, 1977

Hour CST	Cases		Calms		10-30°		40-60°		70-90°		100-120°		130-150°		160-180°		190-210°		220-240°		250-270°		280-300°		300-330°		340-360°	
	All	Less Calms	No.	% All Cases	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
00	86	66	20	30.3	9	13.6	3	4.5	1	1.5	0	0.0	0	0.0	2	3.0	37	56.0	1	1.5	3	4.5	1	1.5	2	3.0	7	10.6
01	86	61	25	40.9	9	14.8	4	6.6	0	0.0	1	1.6	0	0.0	2	3.3	31	50.8	5	8.2	1	1.6	0	0.0	3	4.9	5	8.2
02	86	66	20	30.3	10	15.2	4	6.1	1	1.5	0	0.0	0	0.0	1	1.5	29	43.9	2	3.0	2	3.0	2	3.0	5	7.6	10	15.2
03	86	61	25	40.9	14	23.0	2	3.3	0	0.0	1	1.6	0	0.0	3	4.9	24	39.3	3	4.9	3	4.9	1	1.6	4	6.6	6	9.8
04	86	61	25	40.9	15	24.6	2	3.3	3	4.9	0	0.0	1	1.6	5	8.2	21	34.4	3	4.9	2	3.3	2	3.3	1	1.6	6	9.8
05	86	66	20	30.3	11	16.7	7	10.6	2	3.0	0	0.0	1	1.5	2	3.0	26	39.4	0	0.0	2	3.0	3	4.5	2	3.0	10	15.2
06	86	67	19	28.4	15	22.4	5	7.5	3	4.5	0	0.0	1	1.5	8	11.9	27	40.3	2	3.0	1	1.5	0	0.0	1	1.5	4	6.0
07	86	68	8	11.8	11	16.2	9	13.2	4	5.9	3	4.4	3	4.4	13	19.1	31	45.6	1	1.5	0	0.0	0	0.0	0	0.0	3	4.4
08	86	81	5	6.2	9	11.1	5	6.2	5	6.2	2	2.5	5	6.2	15	18.5	37	45.7	0	0.0	1	1.2	0	0.0	1	1.2	1	1.2
09	86	85	1	1.2	9	10.6	6	7.1	5	5.9	3	3.5	3	3.5	15	17.6	37	43.5	4	4.7	0	0.0	1	1.2	2	2.4	0	0.0
10	87	87	0	0.0	7	8.0	6	6.9	7	8.0	3	3.4	4	4.6	9	10.3	39	44.8	5	5.7	2	2.3	3	3.4	2	2.3	0	0.0
11	87	87	0	0.0	6	6.9	10	11.5	3	3.4	4	4.6	5	5.7	7	8.0	40	46.0	5	5.7	1	1.1	2	2.3	2	2.3	2	2.3
12	86	86	0	0.0	4	4.6	7	8.1	5	5.8	4	4.6	5	5.8	12	13.9	39	45.3	2	2.3	2	2.3	2	2.3	3	3.5	1	1.2
13	86	86	0	0.0	4	4.7	7	8.1	4	4.7	5	5.8	5	5.8	13	15.1	38	44.2	1	1.2	3	3.5	3	3.5	1	1.2	2	2.3
14	87	87	0	0.0	6	6.9	5	5.7	7	8.0	7	8.0	3	3.4	14	16.1	39	44.8	3	3.4	0	0.0	2	2.3	1	1.1	0	0.0
15	86	86	0	0.0	7	8.1	7	8.1	5	5.8	3	3.5	4	4.7	17	19.8	38	44.2	1	1.2	0	0.0	2	2.3	2	2.3	0	0.0
16	86	86	0	0.0	6	7.0	4	4.7	7	8.1	2	2.3	7	8.1	14	16.3	37	43.0	2	2.3	0	0.0	2	2.3	3	3.5	2	2.3
17	86	86	0	0.0	11	12.8	3	3.5	4	4.7	6	7.0	5	5.8	13	15.1	36	41.9	3	3.5	1	1.2	0	0.0	2	2.3	2	2.3
18	86	81	5	6.2	4	4.9	9	11.1	6	7.4	4	4.9	4	4.9	12	14.8	38	46.9	0	0.0	2	2.5	0	0.0	2	2.5	0	0.0
19	86	78	8	10.3	5	6.4	8	10.3	5	6.4	2	2.6	3	3.8	16	20.5	32	41.0	5	6.4	0	0.0	0	0.0	0	0.0	2	2.6
20	86	76	10	13.2	8	10.5	6	7.9	3	3.9	3	3.9	0	0.0	11	14.5	37	48.7	4	5.3	0	0.0	2	2.6	1	1.3	1	1.3
21	86	72	14	19.4	7	9.7	8	11.1	2	2.8	0	0.0	3	4.2	6	8.3	38	52.8	1	1.4	1	1.4	0	0.0	2	2.8	4	5.6
22	86	70	16	22.9	7	10.0	5	7.1	2	2.9	1	1.4	3	4.3	6	8.6	35	50.0	1	1.4	1	1.4	1	1.4	4	5.7	4	5.7
23	86	71	15	21.1	5	7.0	8	11.3	0	0.0	0	0.0	0	0.0	5	7.0	38	53.5	4	5.6	2	2.8	1	1.4	4	5.6	4	5.6

Table 6.31. Hourly frequencies of wind speed for Liberty Mounds. July-September, 1977

Hour, CST	0.0 - 0.9 mph		1.0 - 5.9 mph		6.0 - 10.9 mph		11.0 - 15.9 mph		16.0 - 20.9 mph		21.0 - mph		Total
	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values
00	4	4.9	57	70.4	15	18.5	4	4.9	1	1.2	0	0	81
01	5	6.2	53	65.4	17	21.0	5	6.2	1	1.2	0	0	81
02	1	1.2	54	66.7	18	22.2	7	8.6	1	1.2	0	0	81
03	1	1.2	59	72.8	16	19.8	4	4.9	1	1.2	0	0	81
04	2	2.5	59	72.8	16	19.8	4	4.9	0	0.0	0	0	81
05	3	3.7	58	71.6	15	18.5	5	6.2	0	0.0	0	0	81
06	1	1.2	61	75.3	16	19.8	3	3.7	0	0.0	0	0	81
07	4	4.9	51	63.0	22	27.2	3	3.7	1	1.2	0	0	81
08	3	3.7	49	59.8	25	30.5	4	4.9	1	1.0	0	0	82
09	2	2.4	41	50.0	31	37.8	8	9.8	0	0.0	0	0	82
10	2	2.5	34	42.0	30	37.0	13	16.0	2	2.5	0	0	81
11	1	1.2	31	38.3	32	39.5	16	19.8	1	1.2	0	0	81
12	0	0.0	21	25.3	43	51.8	14	16.9	5	6.0	0	0	83
13	0	0.0	23	27.7	44	53.0	11	13.3	5	6.0	0	0	83
14	0	0.0	23	27.7	42	50.6	14	16.9	4	4.8	0	0	83
15	0	0.0	25	30.1	37	44.6	15	18.1	6	7.2	0	0	83
16	0	0.0	27	32.5	36	43.9	14	17.1	5	6.1	0	0	82
17	0	0.0	20	24.0	44	53.0	16	19.3	3	3.6	0	0	83
18	0	0.0	23	27.7	45	54.2	13	15.7	2	2.4	0	0	83
19	0	0.0	23	28.0	45	54.9	13	15.9	1	1.2	0	0	82
20	0	0.0	39	47.6	33	40.2	9	11.0	1	1.2	0	0	82
21	0	0.0	49	59.8	26	31.7	7	8.5	0	0.0	0	0	82
22	2	2.4	48	58.5	27	32.9	5	6.1	0	0.0	0	0	82
23	2	2.4	51	62.2	24	29.3	4	4.9	1	1.2	0	0	82

Table 6.32. Hourly frequencies of wind speed for Tulsa City/County Health Department. July-September, 1977

	0.0 - 0.9 mph		1.0 - 5.9 mph		6.0 - 10.9 mph		11.0 - 15.9 mph		16.0 - 20.9 mph		21.0 - mph		Total
Hour, CST	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values
00	0	0.0	28	32.2	38	43.7	15	17.2	5	5.7	1	1.1	87
01	0	0.0	25	28.7	39	44.8	18	20.7	5	5.7	0	0.0	87
02	1	1.1	24	27.6	40	46.0	20	23.0	2	2.3	0	0.0	87
03	0	0.0	26	29.9	42	48.3	17	19.5	2	2.3	0	0.0	87
04	0	0.0	28	32.2	45	51.7	12	13.8	2	2.3	0	0.0	87
05	0	0.0	25	28.7	45	51.7	14	16.1	3	3.4	0	0.0	87
06	0	0.0	30	34.5	40	46.0	15	17.2	2	2.3	0	0.0	87
07	0	0.0	27	31.0	41	47.1	18	20.7	1	1.1	0	0.0	87
08	0	0.0	30	34.5	34	39.1	20	23.0	3	3.4	0	0.0	87
09	0	0.0	26	29.5	37	42.0	20	22.7	5	5.7	0	0.0	88
10	0	0.0	23	26.1	36	40.9	22	25.0	6	6.8	1	1.1	88
11	0	0.0	21	23.9	39	43.8	24	27.3	4	4.5	1	1.1	89
12	0	0.0	21	23.9	37	41.6	24	27.0	4	4.5	3	3.4	89
13	0	0.0	20	22.7	36	40.4	23	25.8	7	7.9	3	3.4	89
14	0	0.0	19	21.3	29	32.6	30	33.7	9	10.1	2	2.2	89
15	0	0.0	16	17.8	33	36.7	29	32.2	10	11.1	2	2.2	90
16	0	0.0	14	15.7	34	38.2	28	31.5	11	12.4	2	2.2	89
17	0	0.0	15	16.9	34	38.2	27	30.3	11	12.4	2	2.2	89
18	0	0.0	14	15.9	33	37.5	36	40.9	5	5.7	0	0.0	88
19	0	0.0	13	14.8	39	44.3	29	33.0	7	8.0	0	0.0	88
20	0	0.0	15	17.2	38	43.7	30	34.5	4	4.6	0	0.0	87
21	0	0.0	20	23.0	43	49.4	20	23.0	4	4.6	0	0.0	87
22	0	0.0	20	23.0	36	41.4	26	29.9	5	5.7	0	0.0	87
23	0	0.0	23	26.4	35	40.2	24	27.6	5	5.7	0	0.0	87

Table 6.33. Hourly frequencies of wind speed for Wynona. July-September 1977.

	0.0 - 0.9 mph		1.0 - 5.9 mph		6.0 - 10.9 mph		11.0 - 15.9 mph		16.0 - 20.9 mph		21.0 - mph		Total
Hour, CST	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values	Percent	No. Values
00	8	9.4	53	62.4	19	22.4	4	4.7	1	1.2	0	0	85
01	8	9.4	54	63.5	18	21.2	5	5.9	0	0.0	0	0	85
02	9	10.6	56	65.9	15	17.6	4	4.7	1	1.2	0	0	85
03	9	10.6	57	67.1	16	18.8	2	2.4	1	1.2	0	0	85
04	7	8.2	59	69.4	17	20.0	2	2.4	0	0.0	0	0	85
05	9	10.6	59	69.4	15	17.6	2	2.4	0	0.0	0	0	85
06	7	8.2	55	64.7	18	21.2	5	5.9	0	0.0	0	0	85
07	1	1.2	48	57.1	27	32.1	8	9.5	0	0.0	0	0	84
08	0	0.0	39	46.4	27	32.1	17	20.2	1	1.2	0	0	84
09	0	0.0	38	46.3	25	30.5	18	41.5	1	1.2	0	0	82
10	0	0.0	30	36.6	34	41.5	13	15.9	5	6.1	0	0	82
11	0	0.0	25	30.1	38	45.8	16	19.3	4	4.8	0	0	83
12	0	0.0	29	34.9	33	39.8	17	20.5	4	4.8	0	0	83
13	0	0.0	27	32.5	32	38.6	18	21.7	6	7.2	0	0	83
14	0	0.0	23	27.7	37	44.6	18	21.7	5	6.0	0	0	83
15	0	0.0	23	27.7	37	44.6	19	22.9	4	4.8	0	0	83
16	0	0.0	28	33.3	32	38.1	20	23.8	4	4.8	0	0	84
17	0	0.0	33	39.3	28	33.3	20	23.8	3	3.6	0	0	84
18	1	1.2	34	41.0	36	43.4	12	14.5	1	1.2	0	0	83
19	4	5.0	49	61.3	23	28.8	8	10.0	0	0.0	0	0	80
20	5	6.3	53	67.1	23	29.1	3	3.8	0	0.0	0	0	79
21	7	9.1	49	63.6	23	29.9	5	6.5	0	0.0	0	0	77
22	6	7.5	55	68.8	19	23.8	4	5.0	0	0.0	0	0	80
23	9	12.0	53	70.7	17	22.7	4	5.3	1	0.0	0	0	75

Table 6.34. Hourly frequencies of wind speed for Ochelata. July-September, 1977

Hour, CST	0.0 - 0.9 mph No. Values	0.0 - 0.9 mph Percent	1.0 - 5.9 mph No. Values	1.0 - 5.9 mph Percent	6.0 - 10.9 mph No. Values	6.0 - 10.9 mph Percent	11.0 - 15.9 mph No. Values	11.0 - 15.9 mph Percent	16.0 - 20.9 mph No. Values	16.0 - 20.9 mph Percent	21.0 - mph No. Values	21.0 - mph Percent	Total No. Values
00	15	20.5	43	58.9	15	20.5	0	0.0	0	0.0	0	0	73
01	21	28.8	37	50.7	15	20.5	0	0.0	0	0.0	0	0	73
02	17	23.6	43	59.7	12	16.7	0	0.0	0	0.0	0	0	72
03	18	24.7	50	68.5	5	6.8	0	0.0	0	0.0	0	0	73
04	16	21.9	51	69.9	6	8.2	0	0.0	0	0.0	0	0	73
05	17	23.3	49	67.1	7	9.6	0	0.0	0	0.0	0	0	73
06	13	17.8	51	69.9	9	12.3	0	0.0	0	0.0	0	0	73
07	5	6.8	58	79.5	10	13.7	0	0.0	0	0.0	0	0	73
08	4	5.5	57	78.1	10	13.7	2	2.7	0	0.0	0	0	73
09	1	1.4	52	71.2	17	23.3	3	4.1	0	0.0	0	0	73
10	0	0.0	47	64.4	24	32.9	2	2.7	0	0.0	0	0	73
11	0	0.0	43	59.7	26	36.1	3	4.2	0	0.0	0	0	72
12	0	0.0	45	60.8	27	36.5	1	1.4	1	1.4	0	0	74
13	0	0.0	41	55.4	31	41.9	2	2.7	0	0.0	0	0	74
14	0	0.0	37	50.0	36	48.6	1	1.4	0	0.0	0	0	74
15	0	0.0	42	57.5	30	41.1	1	1.4	0	0.0	0	0	73
16	0	0.0	38	52.1	32	43.8	3	4.1	0	0.0	0	0	73
17	0	0.0	39	54.2	32	44.4	1	1.4	0	0.0	0	0	72
18	3	4.1	44	60.3	26	36.1	0	0.0	0	0.0	0	0	73
19	5	6.8	50	68.5	17	23.3	1	1.4	0	0.0	0	0	73
20	8	11.0	45	61.6	20	27.4	0	0.0	0	0.0	0	0	73
21	12	16.4	46	63.0	15	20.5	0	0.0	0	0.0	0	0	73
22	13	17.8	45	61.6	15	20.5	0	0.0	0	0.0	0	0	73
23	12	16.7	45	62.5	15	20.8	0	0.0	0	0.0	0	0	72

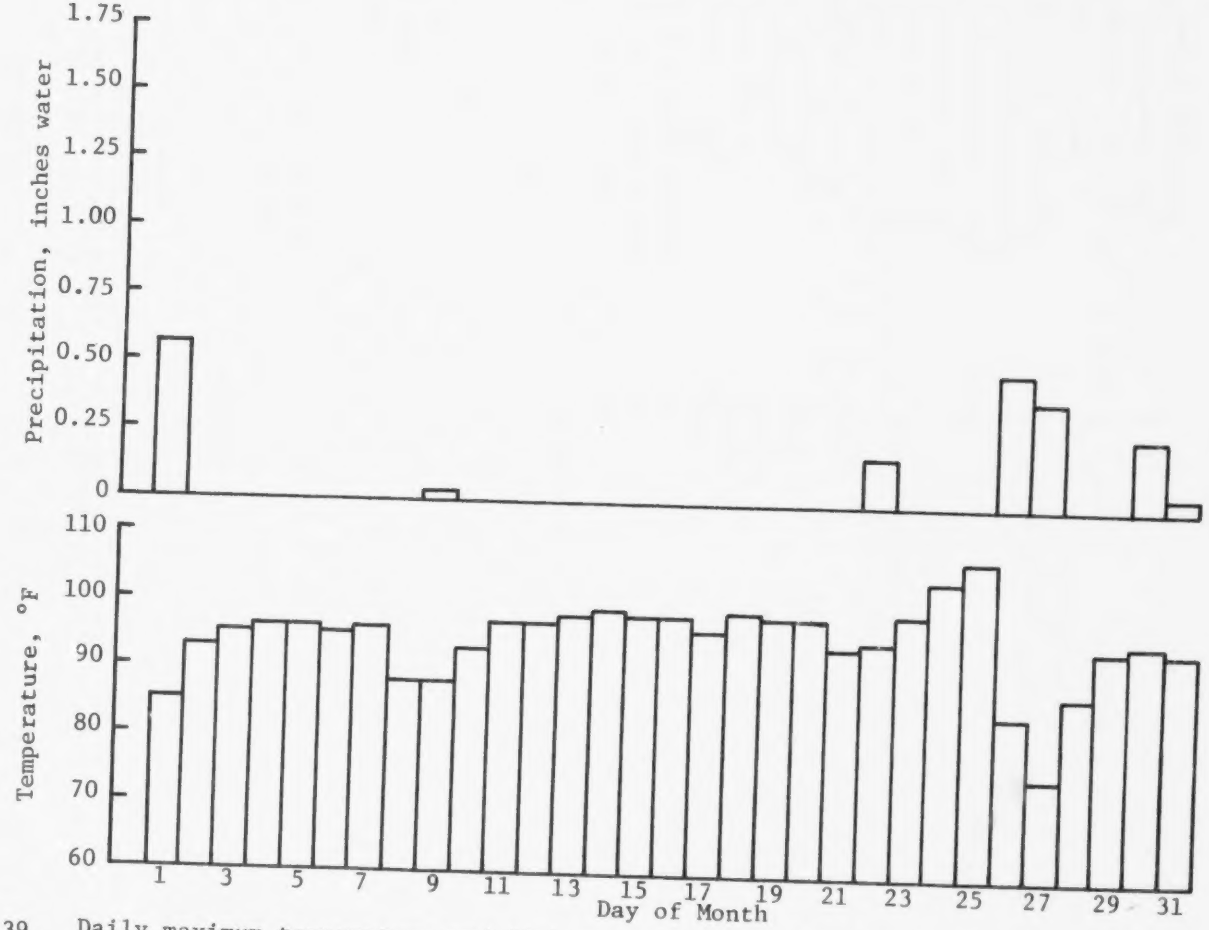

Figure 6.39. Daily maximum temperature and 24-hour total precipitation, Tulsa International Airport, July, 1977. Data supplied by NOAA, Tulsa.

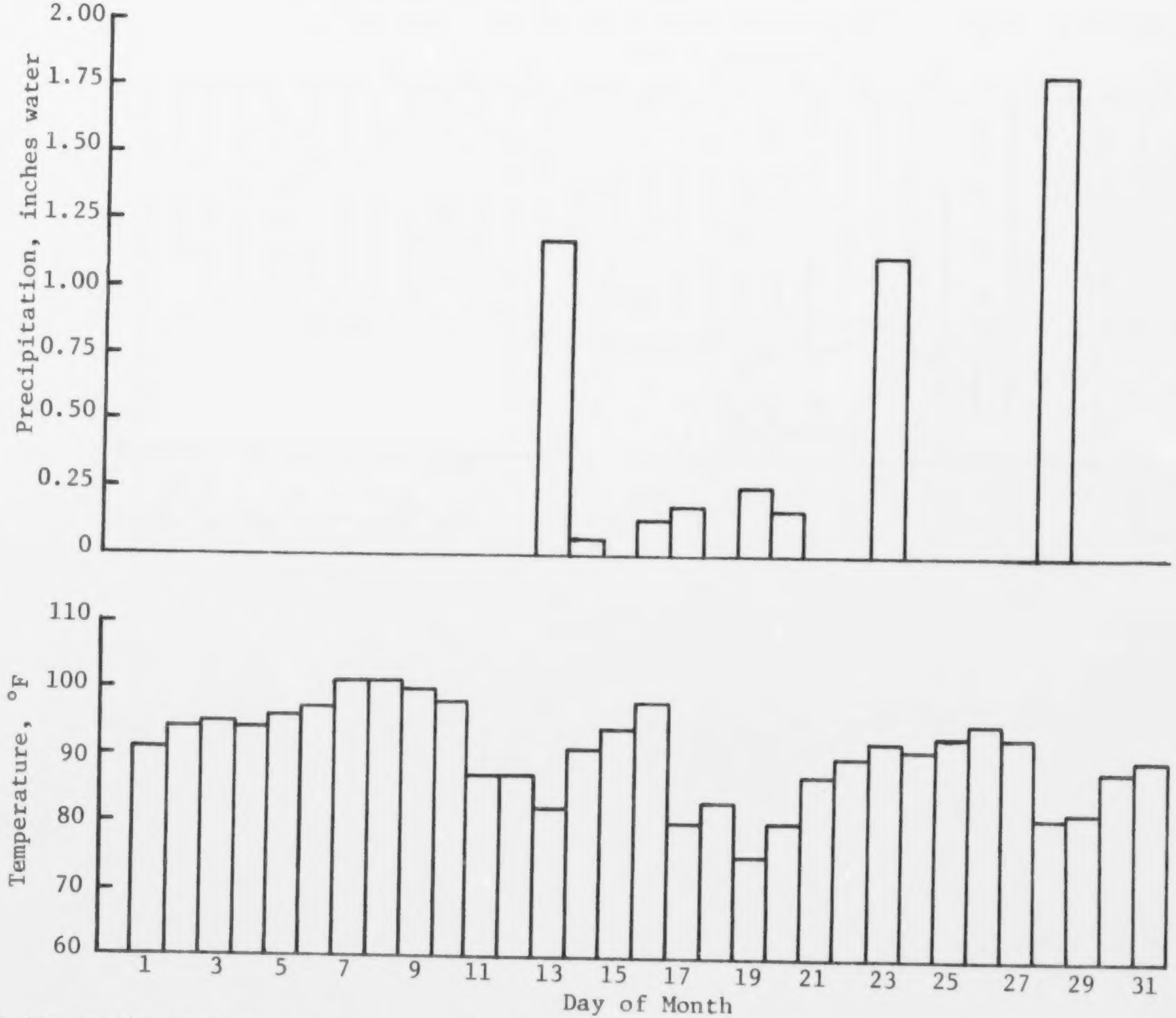

Figure 6.40. Daily maximum temperature and 24-hour total precipitation, Tulsa International Airport, August, 1977. Data supplied by NOAA, Tulsa.

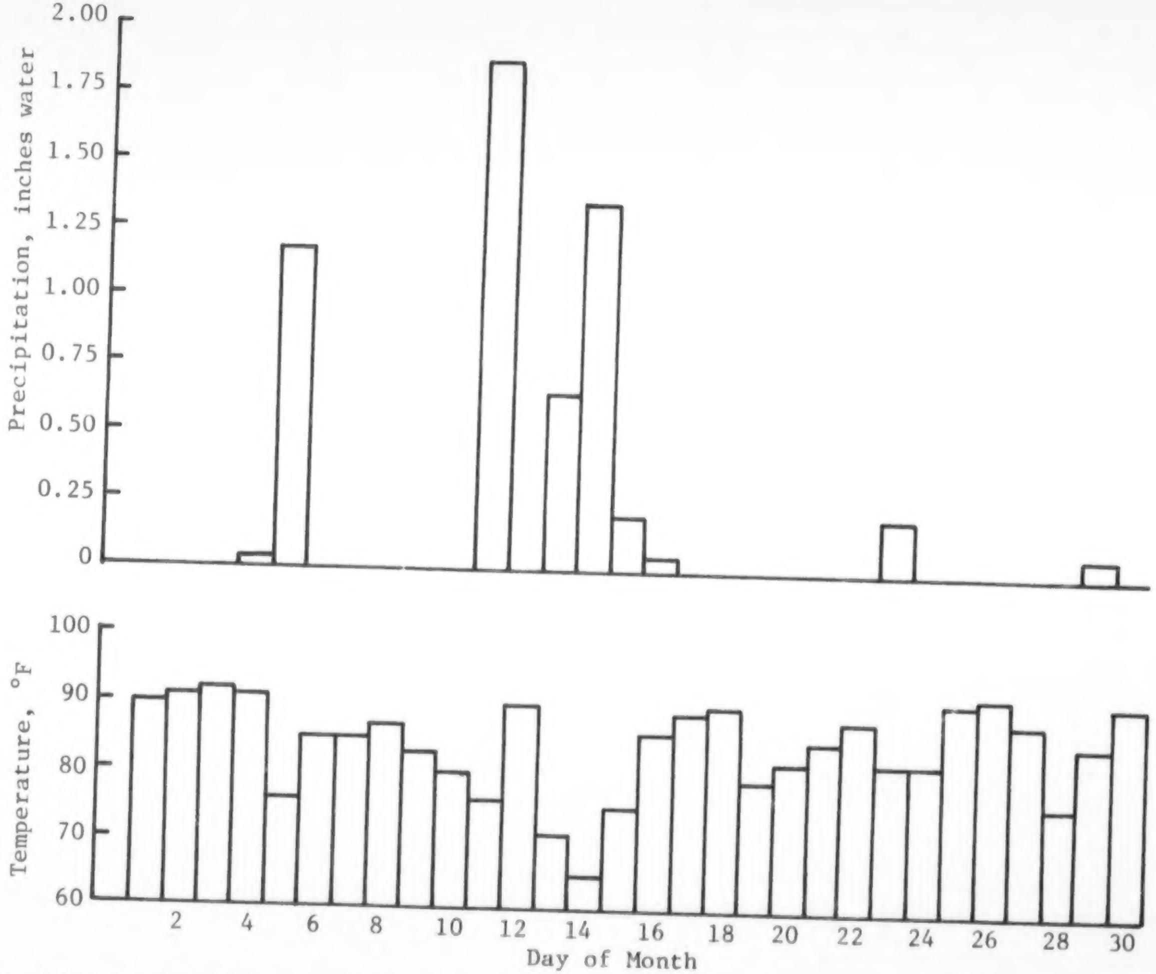

Figure 6.41. Daily maximum temperature and 24-hour total precipitation, Tulsa International Airport, September, 1977. Data supplied by NOAA, Tulsa.

Table 6.35. Average concentrations, ppbC, alkane hydrocarbon species, 0600 to 0900 CDT, Tulsa, Oklahoma, monitoring sites

Compound class	Site					
	Liberty Mounds		Health Department		Post Office	
	Value, ppbC	No. samples	Value, ppbC	No. samples	Value, ppbC	No. samples
Alkane						
Ethane	36.4	70	26.5	77	39.8	78
Propane	54.9	63	23.1	77	38.9	78
Isobutane	11.4	70	10.9	77	24.8	78
n-Butane	25.7	70	26.6	77	69.3	78
Isopentane	17.4	69	31.3	76	58.8	78
n-Pentane + Cyclopentane	36.3	68	39.1	73	41.5	78
2,2-Dimethylbutane	0.0	62	0.1	65	0.2	73
2-Methylpentane	4.0	31	8.5	49	11.6	70
3-Methylpentane	9.1	31	17.7	52	17.7	71
n-Hexane	3.1	61	5.5	69	10.4	74
2,4-Dimethylpentane	0.4	60	0.6	61	1.1	71
2-Methylhexane	1.5	56	5.7	65	7.9	73
3-Methylhexane	1.0	58	4.4	61	4.6	69
2,2,4-Trimethylpentane	1.7	45	4.8	56	8.3	63
n-Heptane	0.7	55	3.1	63	5.1	69
Methylcyclohexane	0.5	41	2.1	60	1.6	62
2,3,4-Trimethylpentane	0.3	54	0.3	63	0.8	69
2-Methylheptane	2.6	56	8.9	71	13.8	71
3-Methylheptane	0.4	59	1.1	71	2.7	71
n-Octane	0.5	61	2.0	71	2.8	74
n-Nonane	0.2	63	0.3	71	1.2	74
n-Decane	0.0	62	0.0	71	0.2	74
n-Undecane	0.0	63	0.0	71	0.0	74
n-Dodecane	0.0	63	0.0	69	0.0	73

Table 6.36. Average concentrations, ppbC, alkene, alkyne, and aromatic hydrocarbon species, 0600 to 0900 CDT, Tulsa, Oklahoma, monitoring sites

Compound class	Site					
	Liberty Mounds		Health Department		Post Office	
	Value, ppbC	No. samples	Value, ppbC	No. samples	Value, ppbC	No. samples
Alkene						
Ethylene	(a)	(a)	22.2	72	45.0	78
Propylene	4.2	70	7.3	77	10.7	78
t-2-Pentene + Isoprene	1.6	61	2.3	71	3.4	74
1-Hexene	0.2	61	0.1	68	0.6	70
β-Pinene	0.0	67	0.0	72	0.0	76
Aromatic						
Benzene	15.3	66	23.8	73	29.6	76
Toluene	7.3	66	9.5	73	13.8	76
Ethylbenzene	3.4	65	5.9	72	3.9	76
p-Xylene + α-Pinene	0.8	66	0.9	72	2.0	76
m-Xylene	1.4	66	2.4	72	4.7	76
o-Xylene	0.8	65	1.7	72	2.9	76
n-Propylbenzene	3.1	66	2.1	72	2.9	76
m-Ethyltoluene	1.0	66	0.7	72	1.7	76
1,3,5-Trimethylbenzene	1.0	66	0.6	72	1.8	76
t-Butylbenzene	0.8	66	0.1	72	1.0	76
o-Ethyltoluene	0.8	66	0.3	72	1.0	76
1,2,4-Trimethylbenzene	9.4	66	11.0	72	18.5	76
1,2,3-Trimethylbenzene	1.0	66	1.0	72	3.4	76
n-Butylbenzene	0.9	66	1.9	72	5.0	76
Alkyne						
Acetylene	2.1	70	11.8	77	18.5	78

(a)Invalid data; no computation.

6.6 TENAX GC/MS/COMP RESULTS

The results obtained from the collection and analysis of volatile organics by Tenax GC/MS/COMP are presented in tables and figures in Volume II of this report. The ambient air sampling protocol for collection of the five samples is given in Table 3.3 of this volume.

In these five samples, over 100 compounds were detected and identified. The composition consisted of an assortment of alkanes, alkenes, alkyl aromatics, oxygenated compounds, halogenated hydrocarbons, and nitrogen-containing substances. A general inspection of the profiles indicates a substantial increase in the overall quantity of constituents between the sample collected at Liberty Mounds and at the downtown Tulsa Post Office. The chromatographic conditions used for the resolution of the constituents in these samples were not precisely controlled and thus make it difficult to compare samples on a quantitative basis.

Table 6.37 presents the quantitative comparison of volatile organics that was made for ambient air 0600 to 0900 CDT samples from Liberty Mounds and the Tulsa Post Office site, and a 1400 to 1700 CDT sample from Vera. A significant increase in the relative quantity of alkanes, alkenes, alkyl aromatics (including benzene and toluene) and ketones occurs as the ambient air is transported from Liberty Mounds through downtown Tulsa. Then the concentrations decrease upon reaching Vera.

In Volume III of this report, results of the Tenax GC/MS/COMP samples are compared with those obtained from samples collected in stainless steel cylinders and analyzed by GC/FID.

Table 6.37. Quantitative comparison of volatile organics in ambient air from Liberty Mounds, Tulsa, and Vera. GC/MS analysis

	Site		
Chemical Class	Liberty Mounds	Post Office, Tulsa	Vera
alkanes ($\geq C_6$)	4.61 ± 0.28	15.92 ± 1.15 (3.4)[a]	6.87 ± 0.74 (1.5)
alkenes ($\geq C_6$)	4.56 ± 0.06	11.67 ± 1.20 (2.5)	5.79 ± 0.59 (1.3)
alkyl aromatics ($\geq C_8$)	3.36 ± 0.62	10.82 ± 0.99 (3.2)	3.64 ± 1.18 (1.1)
benzene	0.25 ± 0.13	0.43 ± 0.01 (1.7)	0.10 ± 0.01 (0.4)
toluene	0.43 ± 0.10	3.74 ± 0.46 (8.7)	0.29 ± 0.03 (0.7)
aldehydes ($\geq C_6$)	3.60 ± 0.46	1.36 ± 0.07 (0.38)	0.72 ± 0.28 (0.2)
ketones ($\geq C_3$)	0.51 ± 0.06	1.74 ± 0.20 (3.4)	0.13 ± 0.5 (0.2)
phenols ($\geq C_7$)	2.34 ± 0.26	1.38 ± 0.03 (0.6)	1.82 ± 0.46 (0.7)
misc. oxygenates ($\geq C_4$)	1.91 ± 0.39	0.89 ± 0.51 (0.5)	0.87 ± 0.30 (0.5)
light hydrocarbons (C_3-C_5)	0.81 ± 0.07	0.39 ± 0.06 (0.5)	0.12 ± 0.07 (0.1)

[a] Values in arbitrary units/m^3 of air, numbers in parenthesis relative to Liberty Mounds.

SECTION 7.0

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APPENDIX A

SAMPLING AND ANALYTICAL METHODOLOGY FOR GC-FID IDENTIFICATION OF HYDROCARBONS

APPENDIX A

SAMPLING AND ANALYTICAL METHODOLOGY FOR GC-FID IDENTIFICATION OF HYDROCARBONS

RTI provided sample containers for the collection of ambient air samples for subsequent analyses of trace organic volatiles. Samples were collected at selected sites within the Tulsa study area. The overall methodology can be broken down into two basic areas: (1) the collection of air samples, and (2) the analysis of the air samples. These two are discussed in the following subsections.

1.0 Sampling Criteria

Obtaining a representative air sample for analysis of trace organic volatiles is not a trivial task. Three factors must be considered.

1. The air sample must be representative of the air mass. Two approaches can be used to accomplish this goal. The first is to collect a multitude of short-term grab samples; the second is to collect longer term integrated samples. From previous field experience, the latter approach provides less erratic data than the former.
2. In order to characterize an area for its hydrocarbon background, samples have to be collected at appropriate sites and times. For example, if samples are collected between 6:00 and 9:00 a.m. LDT in an urban center, the data will be strongly influenced by automotive emissions. It would be difficult to determine the contributions of other hydrocarbon emission sources to the urban air mass. Total characterization of sources can only be accomplished by collecting samples at different times of the day so that one emission source does not predominately influence the hydrocarbon background.
3. The sample must not be altered by either the collection device or the sampling containers. This aspect has been evaluated in RTI laboratories and our findings will be discussed in the next sections.

1.1 Sampling Containers

A variety of sampling techniques have been employed to collect trace hydrocarbon species, but two methods have prevailed. One involves the collection of trace volatiles on a solid adsorbent. The other involves collecting a volume of air inside a container, then concentrating a part of that sample to analyze for the trace constituents. RTI has had a great deal of experience in both areas. Samples for GC/MS analyses were collected on Tenax GC (refer to Appendix B) while samples for GC/FID, GC/EC were collected in treated stainless steel containers.

1.1.1 Construction and Leak Checking Stainless Containers

The containers utilized in this study were constructed of all stainless steel components. The bodies of the containers as well as the tops were made from 304 stainless steel. The container bodies were constructed from a 2-l stainless steel beaker manufactured by Vollrath (Sheboygan, Wisconsin). The tops of the containers were stamped from 304, 1/8" thick stainless steel. The lips on the stainless steel beakers were cut with a wet cutting wheel after the container had been electropolished. After the container was cut it was cleaned with strong oxidizing reagents to remove any grease deposits on the inside of the container.

A 1/4" x 2" stainless steel tube was heliarced to the top of each container. The tops were then electropolished, and the tops and bodies of the containers were joined by heliarcing under an inert atmosphere to prevent any oxidation of the interior surfaces during this process. The containers were then mounted with H series Nupro valves, constructed of stainless steel with metal bellow seals. Each container was then engraved with a letter and number. The letter told the function of the container, e.g., source sampling or ambient sampling, and the number identified the container.

The container was then ready for testing. It was first pressurized to 60 psi with zero air and leak checked under pressure. The container was immersed in clear water and visually inspected for leaks. If there were no leaks, the container was ready to be cleaned.

1.1.2 Cleaning Procedure for Stainless Steel Containers

The cleanup procedure for a new sample container being put into service for the first time was identical to that for a container which was returned from the field. First, the container is evacuated to less than 0.5 mm Hg pressure. The bellows valve is closed and torqued to 20 in-lb. This 20 in-lb torquing is repeated each time the valve is closed. Next, the container was loosely connected to the clean air supply, and the compression fitting connections were flushed with clean air. After approximately 1 min, the compression fitting connection was tightened and the container valve opened. When the container was pressurized to 60 psi, the valve was torqued closed and the container was disconnected from the zero air supply. The container was allowed to equilibrate for 20 minutes, then heated to approximately 100° C and evacuated. The pressurization heat/evacuation process was repeated. The bellows valves were torqued shut, and the container inlet port was finally sealed with a brass plug to prevent any loss of vacuum. The container was then ready for shipment to the field for sampling.

1.1.3 Shipping Procedure and Logging Procedure for Stainless Steel Containers

After the container had been cleaned and sealed with a brass plug, a tag containing the following information was attached to the tubing below the valve:

Container No.:
Sampling Date:
Sampling Starting Time:
Sampling Finishing Time:
Site:
Flow Rate - Start: Finish:

The container number was entered prior to shipping; the rest of the data was entered by the sampling team. Sampling data, time and site are self-explanatory. The flow rates were measured by attaching a soap film flow meter to the end of the critical orifice while the pump was drawing in air from the manifold. The starting flow rate was measured just prior to attaching the sample container; the finish flow rate was taken immediately after the container was removed. Thus, any large changes in flow rates, which could indicated plugging of the orifice, could be detected.

The containers were packed in aluminum suitcases and shipped air freight to Tulsa. Two couriers were used during the program: Eastern Airlines and Federal Express.

Prior to its departure, each container's number was entered on a master log sheet to enable RTI to keep track of each container's whereabouts. The same log sheet had spaces to record the dates when the containers were returned to RTI and when each analysis was performed.

1.2 Pumping System, Metal Bellows Pump

To collect ambient air samples with the stainless steel containers, various approaches could have been taken. Since the containers were evacuated, they could simply have been opened to the atmosphere and filled. To collect an integrated sample over time, a critical orifice could have been mounted in front of the valve, and the valve opened. The orifice would have maintained a constant flow rate up to 0.5 atmosphere of vacuum, but beyond 0.5 atmosphere the flow rate would no longer have been constant and would gradually fall to zero until the container was filled (i.e., was at ambient pressure). This method has two drawbacks: (1) it does not provide a constant flow rate during the entire sampling period, and (2) it provides samples which are at atmospheric pressure or under a partial vacuum.

To alleviate these problems the container needs to be pressurized. Pressurizing the container without contaminating the sample air can only be accomplished by employing a pump free of lubricants and polymeric diaphrams. The only pump which provides this capability is the metal bellows pump which is constructed of stainless steel and TFE Teflon. Such pumps can deliver pressures of up to 40 psig.

1.2.1 Sampling Methodology Associated with the Stainless Steel Containers

The approach described in Section 1.2 was employed by RTI to collect samples in Tulsa. Figure A.1 is a schematic drawing of the system used. The system consisted of two metal bellows pumps mounted on a 10" x 16" x 3/8" piece of plywood. The piece of plywood was shock mounted with four rubber feet.

The system was constructed to minimize the sample's residence time inside the tubing. In order to pressure the container to 5 psig over a 3-hr period, flow rates had to be approximately 15 ml/min. With a single pump long residence time inside the tubing connecting the MB (Metal Bellows Corporation) pump and the sampling manifold would exist. To minimize the residence time, the MB-21 or MB-41 pump pulled air from the station manifold at an elevated flow

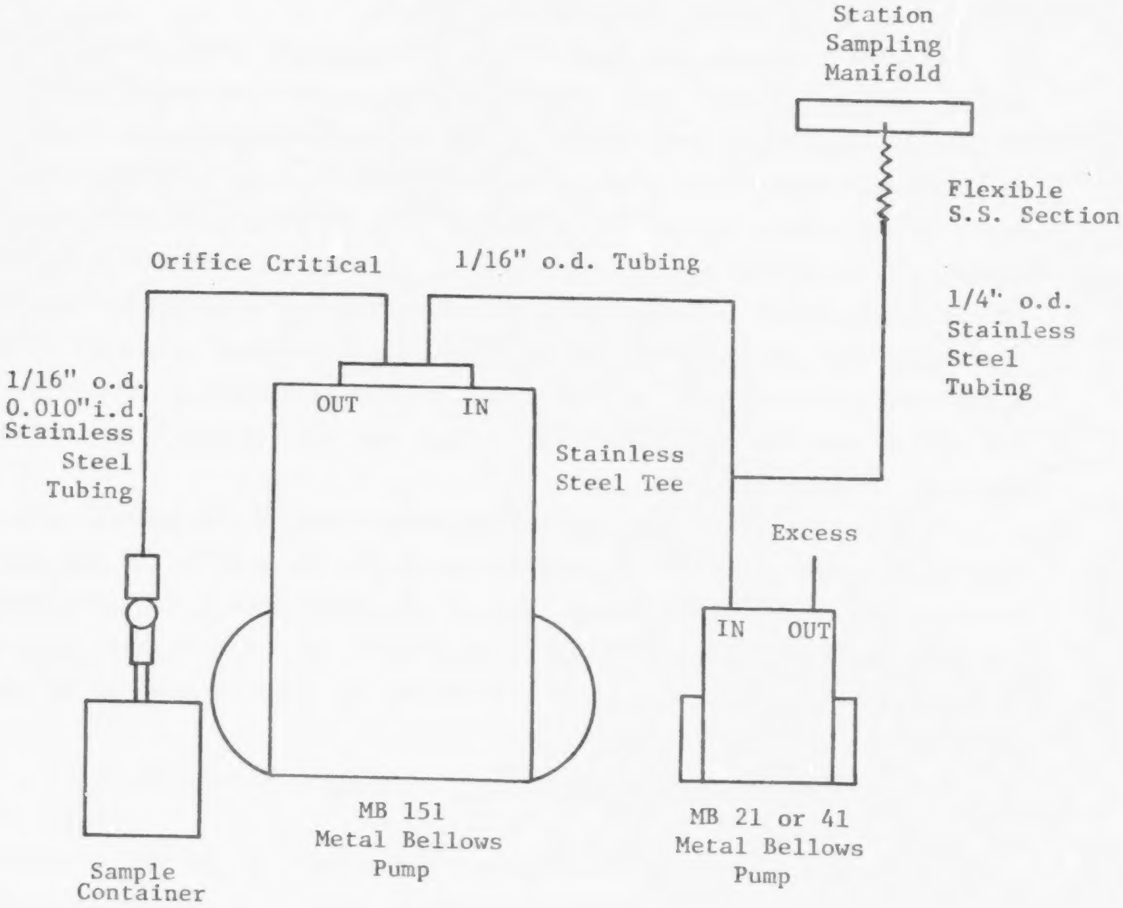

Station
Sampling
Manifold
Flexible
S.S. Section
Orifice Critical
1/16" o.d. Tubing
1/4" o.d.
Stainless
Steel
Tubing
1/16" o.d.
0.010"i.d.
Stainless
Steel
Tubing
OUT
IN
Stainless
Steel Tee
Excess
IN
OUT
MB 151
Metal Bellows
Pump
MB 21 or 41
Metal Bellows
Pump
Sample
Container

Figure A.1. Schematic of RTI's pumping system used to collect field samples.

rate of 2-3 l/min. A stainless steel Swagelok tee connected the MB-151 pump to the station manifold and the smaller metal bellows pump. The small metal bellows pump was attached to the sampling manifold via 1/4" o.d. stainless steel tubing connected to a 12" long piece of flexible stainless steel tubing which absorbed most of the vibrations. All connections were made with Swagelok compression fittings.

The tubing connecting the Swagelok tee to the MB-151 pump was 1/16" o.d., 0.030" i.d., to minimize the internal volume. The tubing connecting the MB-151 and the stainless steel sampling container was 1/16" o.d. x 0.010" i.d. The interior diameter of the tubing was further reduced by crimping the tubing over a 6 - 8" length. This technique cut the flow rate from several hundred ml/min to 10 - 30 ml/min. Prior to field deployment each system was tested. This testing is described in more detail in the next section.

1.2.2 Pumping System Performance Checkout

The first checkout for the pumping system was designed to insure that it was leak free. Leaks in the MB-21 or 41 pumps were not as critical as for the rest of the system, since the only purpose of the smaller pumps was to purge the tubing connecting the MB-151 pump and the manifold. The fittings connecting the MB-151 to the Swagelok tee were checked by plugging each arm of the tee, then monitoring the flow rate at the output of the MB-151 with a soap bubble flow meter. With such an arrangement, leaks of less than 0.1 ml/min could easily be detected. The system was next tested by plugging the outlet of the pump and attaching a bubble flow meter to the inlet. The fittings on top of the pump were tested with a nonorganic base soap material ("Snoop") to check for microscopic leaks.

After this inspection, the critical orifices on each pumping system were tested for proper flow rate over a typical sampling period. Each pumping system was attached to a mass flow meter with its output displayed on a strip chart recorder. Each pumping system was tested for at least 2 hr. During the testing period, it was noted that the flow rate decreased for the first 15 minutes, then stabilized. During this time period the pump attained thermal equilibrium. Therefore, in the field, a 15-min warmup time was used to purge the pumping system prior to beginning sample collection.

Another important test was to insure that a constant flow rate could be maintained throughout the sampling period. An experiment was set up with a mass flow meter in line between the stainless steel container and the critical orifice. The output of the mass flow meter was again displayed on a strip chart recorder. A printout of such a test is shown in Figure A.2.

To check for contamination of the samples by the pumps, and to insure the integrity of the system, the pumping system was attached to RTI's clean air source. The analysis of the pumping system output showed only ethylene, which is shown to be present in the clean air supply at approximately 0.2 ppb.

The final test was to check the effect of the pumping system on a variety of hydrocarbons. A complex mixture of C_5 - C_{10} hydrocarbons was prepared for each compound at 10 -20 ppb (V/V). The mixture was analyzed to ascertain the concentration of each compound. It was then sampled by the pumping system. The output was analyzed, and the concentration of each compound was found to be within the experimental error of the repeatability of the initial analyses. After this test, the pumping systems were ready for field usage.

1.3 Deployment of RTI's Sampling Systems in Tulsa

Five pumping systems and associated critical orifices and stainless steel tubing were provided for the Tulsa study. RTI personnel were trained in the collection of samples with both stainless steel containers and Tenax cartridges.

2.0 Analytical Techniques

In this project, each sample was analyzed for three major groups of compounds: C_2 - C_5 light hydrocarbons; C_5 - C_{12} aliphatics; and C_6 - C_{10} aromatics. A packed column was used for the C_2 - C_5 light hydrocarbons analyses, while the aliphatic and aromatic mixtures were separated on capillary columns. The hydrocarbon compounds were detected by a flame ionization detector (FID). The detector response was transmitted to a Hewlett-Packard Model 18652A analog to digital converter and this signal was then transmitted to a Hewlett-Packard 3352B laboratory data system. All chromatograms were also displayed on Linear Model 225 M or Perkin-Elmer Model 56 strip chart recorders. The Hewlett-Packard data system has capability to store response factors for each individual compound selected as well as identifying compounds on the basis of retention time.

Three analyses, C_2 - C_5, C_5 - C_{10} aliphatic, and C_6 - C_{10} aromatic shared the same pumping system for drawing samples from the sample containers through the cryogenic trap. The pump, a Metal Bellows Corporation model MB 151, was equipped with a critical orifice which controlled the flow rate at 100 ml/min.

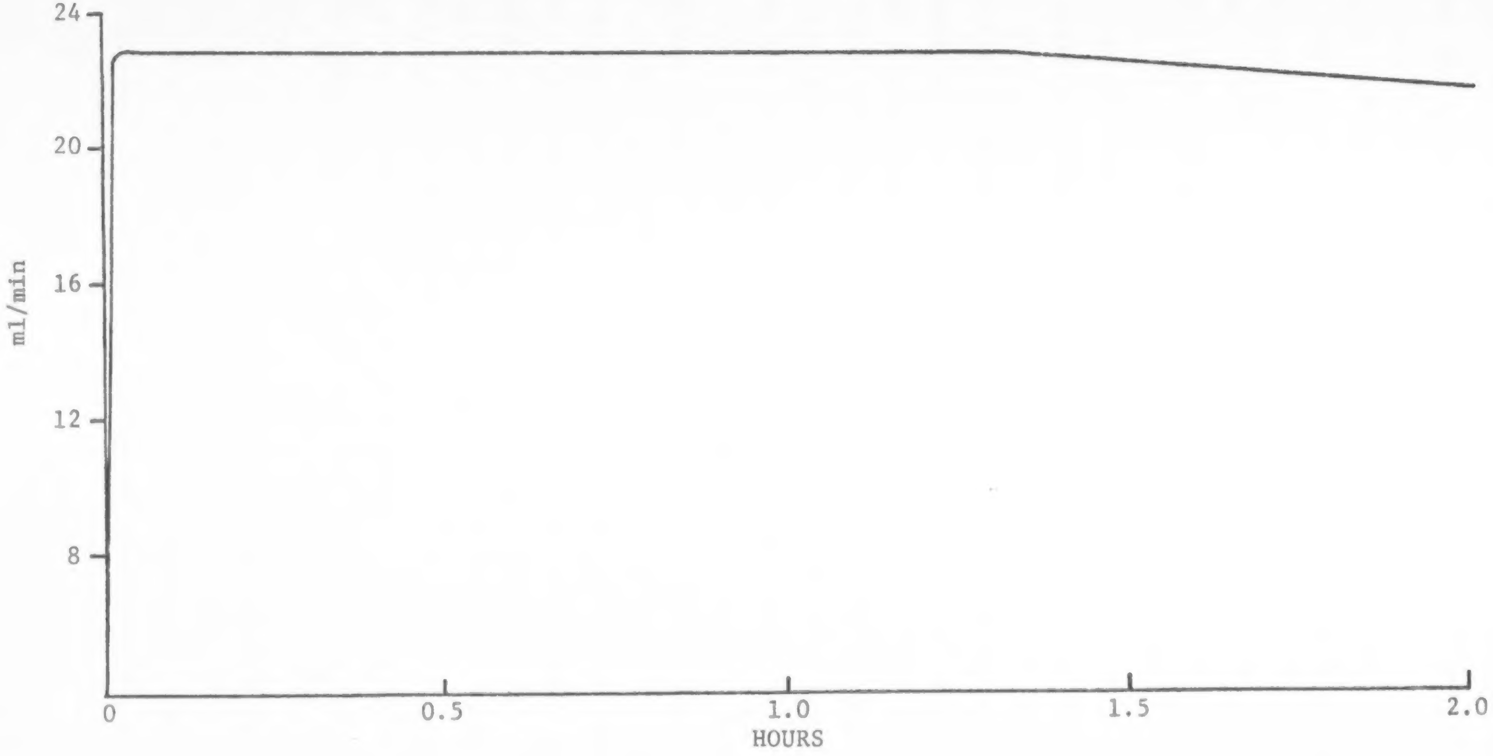


Figure A.2. Flow rate versus time for filling a 2-1 stainless steel container by MB 151 metal bellows pump.

Air from the outlet side of the pump was passed through a 1-l/revolution American Meter Company wet test meter (model 802). The scale was graduated in 10 ml divisions and the meter could easily be read to ±2 ml.

A series of valves on the inlet side of the pump determined which of the three systems would be monitored (see Figure A.3). The outlet side was also controlled by an open-shut valve which prevented a backflow of air into the partially evacuated bellows when the pump was turned off. It was desirable to keep a partial vacuum on the bellows to avoid a lengthy bellows evacuation time prior to the sample withdrawal.

The sampling procedures for these three analyses were similar. First, the sample container was attached to the appropriate system by means of a 1/16" o.d. stainless steel tube. The container was then placed in a heated oven and allowed to reach 60° - 70° C. The pump was turned on and the outlet valve opened to allow the bellows to empty. On the C_2 - C_5 and aromatic analyses, the inlet valve of the container was also opened, since there was another shut-off valve separating the pump from the sample container on these systems. As the pump was emptying, the cryogenic trap was immersed in liquid oxygen and allowed to cool. When the bellows had emptied, as evidenced by the absence of movement on the wet test meter, the valve separating the pump and sample container was opened. Approximately ten milliliters of sample was allowed to bypass the trap in order to flush out the sample lines. Then, with the proper arrangement of the multiport valves, the next 100 ml was routed through the trap. Upon trapping out the desired volume of sample, the pump was switched off and all inlet and outlet valves were closed in quick succession. The multiport valves were then arranged to close off the trap from the rest of the system. The liquid oxygen was removed, and the trap was immersed in a 200° C silicone oil bath. After sufficient time to heat the trap (from 15 sec for C_2 - C_5 to 1.5 - 2 min for aliphatics), the sample was injected and the analysis program commenced.

2.1 C_2 - C_5 Light Hydrocarbons Analysis

The C_2 - C_5 light hydrocarbon analysis system was made up of a Perkin-Elmer model 900 gas chromatograph equipped with an 8' × 1/8" stainless steel column packed with 100-120 mesh Durapak® phenylisocyanate. The column was

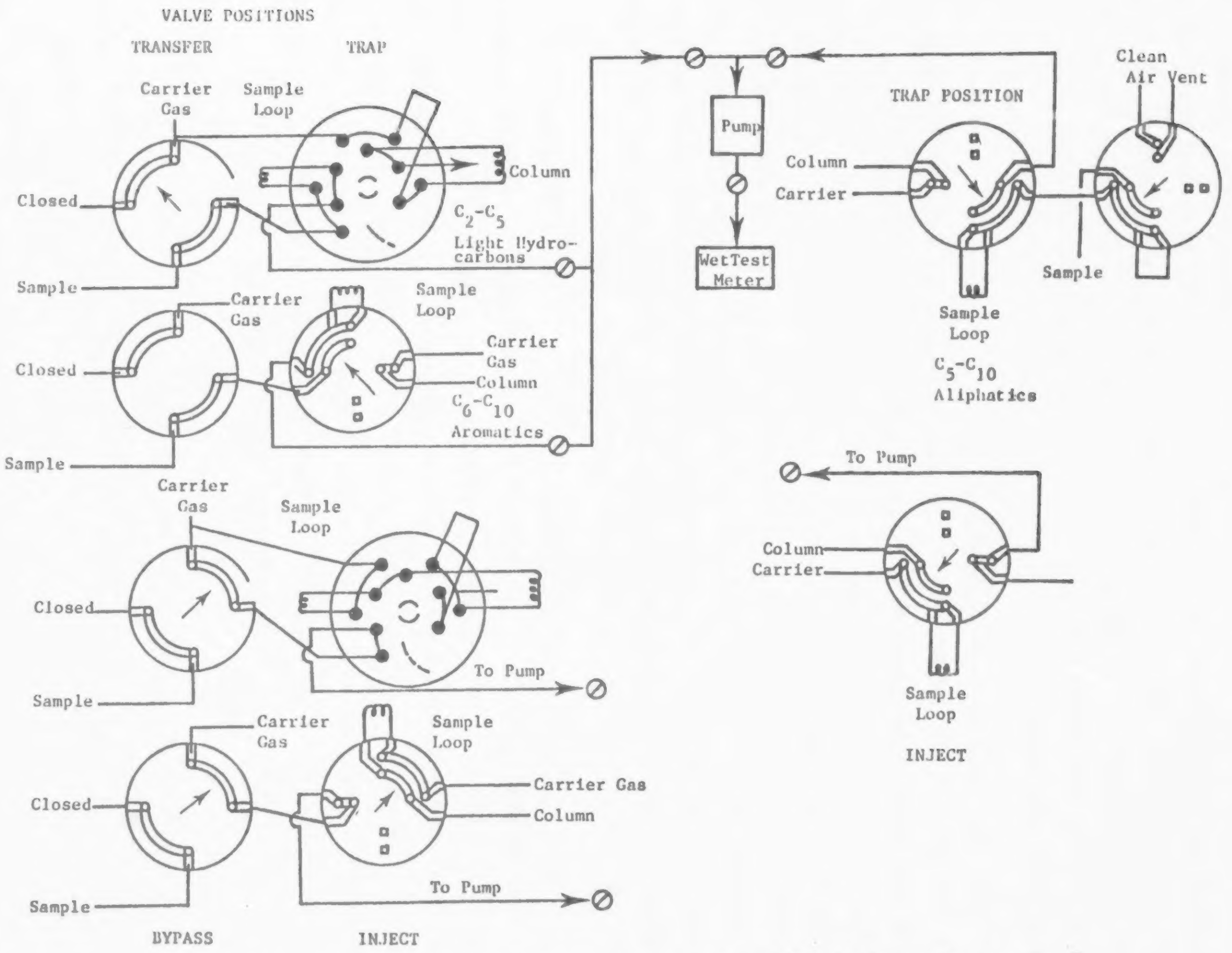

VALVE POSITIONS
TRANSFER
TRAP
Carrier Gas
Sample Loop
Closed
Sample
Column
C_2-C_5 Light Hydrocarbons
Carrier Gas
Sample Loop
Closed
Sample
Carrier Gas
Column
C_6-C_{10} Aromatics
Carrier Gas
Sample Loop
Closed
Sample
To Pump
Carrier Gas
Sample Loop
Closed
Sample
Carrier Gas
Column
To Pump
BYPASS
INJECT
Pump
WetTest Meter
TRAP POSITION
Column
Carrier
Clean Air Vent
Sample
Sample Loop
C_5-C_{10} Aliphatics
To Pump
Column
Carrier
Sample Loop
INJECT

Figure A.3. Schematic diagram of the C_2-C_5 light hydrocarbons, C_5-C_{10} aliphatic, and C_6-C_{10} aromatic valving system.

maintained at 18° C ± 0.5° in a cold water bath. The analysis was terminated after 30 min. Upon completion of the analysis, the multiport valves were turned to the bypass-trap position in order to backflush the column. The backflushing was assumed to be complete when the FID response returned to baseline. This column was capable of separating ethane and ethylene at room temperature. One of the drawbacks of the column is the poor separation between cyclopentane and n-pentane. Since these two compounds were not adequately separated, they were reported as one component.

2.2 C_5 - C_{12} Aliphatic Analyses

The C_5 - C_{12} aliphatic analysis system consisted of a Perkin-Elmer model 3920B gas chromatograph equipped with a 200 ft length SCOT OV-101 capillary column. This capillary column was chosen for its excellent separation of aliphatic compounds in the C_5 - C_{12} molecular weight range. The analysis was started by injecting the sample into the column at 30° C. This temperature was maintained for 8 min, then the column was temperature programmed at a rate of 4° C/min until it reached 100° C. The column was held at this temperature until the analysis was completed. The analysis ran for approximately 60 min; there was no need for backflush afterwards.

2.3 C_6 - C_{10} Aromatic Analyses

The analyses for C_6 - C_{10} aromatic compounds were performed using the same Perkin-Elmer model 900 gas chromatograph as used for the C_2 - C_5 analysis. The aromatic compounds, however, were separated on a 200 ft SCOT MBMA capillary column. The column was maintained at 90° C for 6 minutes, then temperature programmed at 0.5°/min to 110° C. This temperature was held until the analysis was completed. The program ran for approximately 60 min, and no backflush was necessary after the completion of the analysis.

APPENDIX B

SAMPLING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY TENAX GC-MS/COMP

APPENDIX B

SAMPLING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

1.0 Principle of Method

Volatile organic compounds are concentrated from ambient air on Tenax GC in a short glass tube (1-3). Recovery of the volatile organics is accomplished by thermal desorption and purging with helium into a liquid nitrogen cooled nickel capillary trap (1,2,4). Then the vapors are introduced into a high resolution glass gas chromatographic column where the constituents are separated from each other (2,5). Characterization and quantification of the constituents in the sample are accomplished by mass spectrometry either by measuring the intensity of the total ion current signal or mass fragmentography (2,6). The collection and analysis systems are shown in Figure B.1.

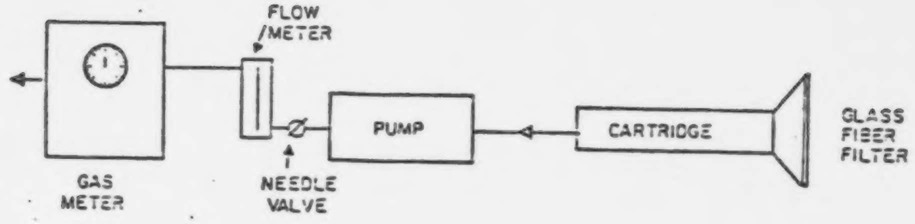
2.0 Range and Sensitivity

The linear range for the analysis of volatile organic compounds depends upon two principal features. The first is a function of the breakthrough volume of each specific compound which is trapped on the Tenax GC sampling cartridge. The second is related to the inherent sensitivity of the mass spectrometer for each organic (2,7). Thus, the range and sensitivity are a direct function of each compound which is present in the original ambient air. The linear range for the quantitation on the gas chromatograph/mass spectrometer/computer (GC/MS/COMP) is generally three orders of magnitude. Table B.1 lists the overall theoretical sensitivity for some examples of volatile organics which is based on these two principles (7).

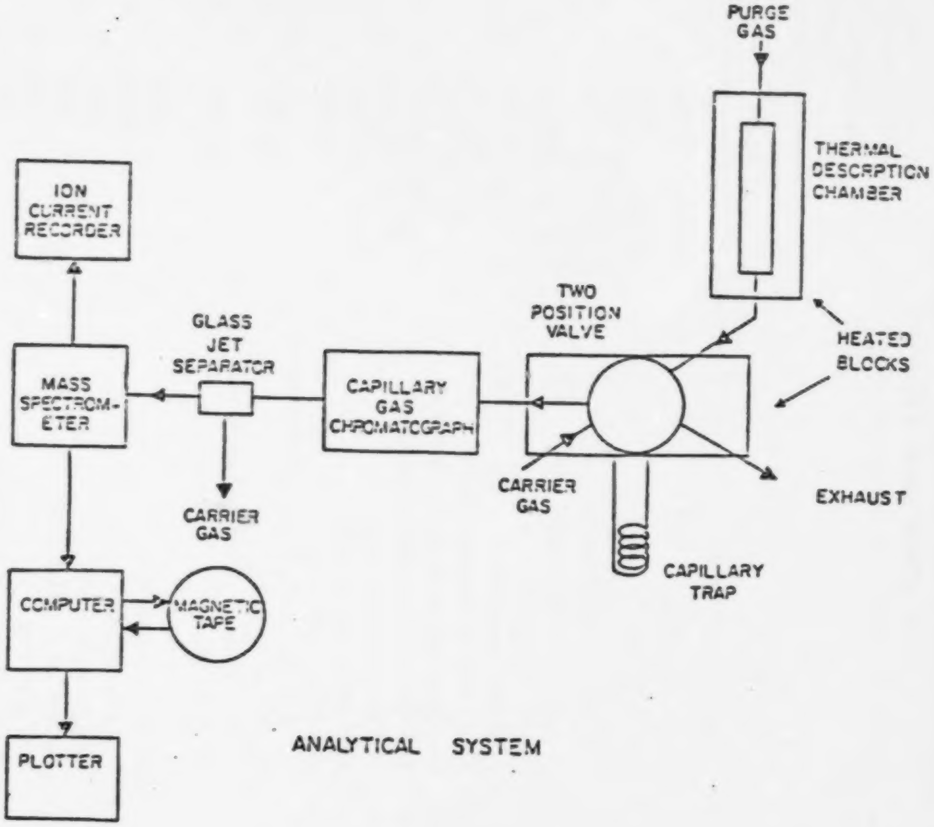
The sensitivity of this technique for the very volatile organic compounds (C_1 to C_5) is inadequate for the purpose of this study. Alternate methods for their collection and analysis are suggested.

3.0 Interferences

The potential difficulties with this technique are primarily associated with those cases where isomeric forms of a particular substance cannot be resolved by the high resolution chromatographic column and at the identical mass cracking pattern of each of the isomers. An example of such a problem is seen with the C_5-alkyl aromatics of which


FLOW
/METER
GAS
METER
NEEDLE
VALVE
PUMP
CARTRIDGE
GLASS
FIBER
FILTER

VAPOR COLLECTION SYSTEM


PURGE
GAS
THERMAL
DESCRPTION
CHAMBER
ION
CURRENT
RECORDER
TWO
POSITION
VALVE
GLASS
JET
SEPARATOR
HEATED
BLOCKS
MASS
SPECTROM-
ETER
CAPILLARY
GAS
CHROMATOGRAPH
CARRIER
GAS
EXHAUST
CARRIER
GAS
CAPILLARY
TRAP
COMPUTER
MAGNETIC
TAPE
PLOTTER

ANALYTICAL SYSTEM

Figure B.1. **Vapor collection and analytical system for analysis of organic vapors in ambient air.**

Table B.1. OVERALL THEORETICAL SENSITIVITY OF HIGH RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER ANALYSIS FOR ATMOSPHERIC POLLUTANTS

Chemical Class		Estimated Detection Limit[a]	
		ng/m^3	ppt
Halogenated hydrocarbon	Vinyl bromide	250	57
	Bromoform	0.340	0.03
	Bromodichloromethane	1.300	0.22
	Dibromochloromethane	0.667	0.07
	1-Bromo-2-chloroethane	1.00	0.67
	Allyl bromide	5.00	1.04
	1-Bromopropane	5.200	1.06
	1-Chloro-3-bromopropane	0.150	0.01
	1-Chloro-2,3-dibromopropane	~0.100	<0.01
	1,1-Dibromo-2-chloropropane	~0.100	<0.01
	1,2-Dibromoethane	0.530	0.07
	1,3-Dibromopropane	~0.100	~0.01
	Epichlorohydrin (1-Chloro-2,3-epoxypropane)	9.600	2.50
	Epibromohydrin (1-Bromo-2,3-epoxypropane)	0.300	0.05
	Bromobenzene	0.100	0.02
	Methyl bromide	500	135
	Methyl chloride	2000	1000
	Vinyl chloride	800	333
	Methylene chloride	700	200
	Chloroform	200	420
	Carbon tetrachloride	250	400

(continued)

Table B.1. (cont'd)

Chemical Class	Compound	Estimated Detection Limit[a] ng/m^3	Estimated Detection Limit[a] ppt
Halogenated hydrocarbon (cont'd)	1,2-Dichloroethane	32	8.15
	1,1,1-Trichloroethane	66	12.45
	Tetrachloroethylene	2.5	0.38
	Trichloroethylene	10	1.92
	1-Chloro-2-methylpropene	62	21.5
	3-Chloro-2-methylpropene	62	21.5
	3-Chloro-1-butene	83	28.8
	Allyl chloride	83	28.8
	4-Chloro-1-butene	38	13.2
	1-Chloro-2-butene	13	4.5
	Chlorobenzene	2.10	0.47
	o-Dichlorobenzene	1.00	0.06
	m-Dichlorobenzene	0.75	0.01
	Benzylchloride	0.65	0.01
Halogenated ethers	2-Chloroethyl ethyl ether	4.15	0.97
	Bis-(chloromethyl)ether	1.0	1.10
Nitrosamines	N-Nitrosodimethylamine	5.0	1.67
	N-Nitrosodiethylamine	3.0	0.74
Oxygenated	Acrolein	~100	56.5
	Glycidaldehyde	~59	19.5
	Propylene oxide	~60	25.5
	Butadiene diepoxide	~20	6.7

(continued)

Table B.1. (cont'd)

Chemical Class	Compound	Estimated Detection Limit[a]	
		ng/m^3	ppt
Oxygenated hydrocarbons (continued)	Cyclohexene oxide	~10	2.5
	Styrene oxide	2	0.415
	Acetophenone	~2	~0.415
	β-Propiolactone	~3	~1.2
Nitrogenous Compounds	Nitromethane	8	~2.4
	Aniline	3.0	0.78
Sulfur Compounds	Diethyl sulfate	~50	-
	Ethyl methane sulfate	~5.0	-

---

[a] Limits are calculated on the basis of the breakthrough volume for 2.2 g of Tenax GC, (at 70°F), capillary column performance and sensitivity of the mass spectrometer to that compound in the mass fragmentography mode of most intense ion.

there are 53 isomers. As the number of carbon atoms increases in the hydrocarbons and aromatics, the number of potential isomers becomes increasingly large and difficult to completely resolve by gas chromatography and and/or by their corresponding mass cracking patterns. However, differentiation between the hydrocarbons; that is alkanes, alkenes, aromatics, oxygenated, etc., can be made.

4.0 Reproducibility

The reproducibility of this method has been determined to range from ±10 to ±30% of the relative standard deviation for different substances when replicate sampling cartridges are examined (5). The inherent analytical errors are a function of several factors: [1] the ability to accurately determine the breakthrough volume for each of the identified organic compounds, [2] the accurate measurement of the ambient air volume sampled, [3] the percent recovery of the organic from the sampling cartridge after a period of storage, [4] the reproducibility of thermal desorption for a compound from the cartridge and its introduction into the analytical system, [5] the accuracy of determining the relative molar response ratios between the identified substance and the external standard used for calibrating the analytical system, [6] the reproducibility of transmitting the sample through the high resolution gas chromatographic column and, [7] the day-to-day reliability of the MS/COMP system (1-8).

The accuracy of analysis is generally ±30%; however, the accuracy of analysis is dependent on the chemical and physical nature of the compound (2,8).

5.0 Advantages and Disadvantages of the Method

The gas chromatograph/mass spectrometer interfaced with a glass jet separator, is extremely sensitive and specific for the analysis of many volatile organic compounds in ambient air. High resolution gas chromatographic separation provides adequate resolution of the substances found in ambient air for the air subsequent quantification. The combination of the high resolution gas chromatographic column and the selection of specific or unique ions representing the various compounds of interest identified in the air samples yields a relatively specific assay method for these compounds (1-8).

Collected samples can be stored up to one month with less than 10% losses for most of the chemical classes (2,8). Because some of the compounds of interest may be hazardous to man, it is extremely important to exercise safety precautions in the preparation and disposal of liquid and gas standards, cleaning of used glassware, etc. in the analysis of air samples.

Since the mass spectrometer cannot be conveniently mobilized, sampling must be carried out away from the instrument.

The efficiency of air sampling increases as the ambient air decreases (i.e., sensitivity increases) (8).

The retention of water by Tenax is low; its thermal stability is high; and its background is negligible allowing sensitivity analysis (1,2,5,8).

6.0 Apparatus

6.1 Sampling Cartridges

The sampling tubes are prepared by packing a ten centimeter long by 1.5 cm i.d. glass tube containing 6 cm of 35/60 mesh Tenax GC with glass wool in the ends to provide support (2,5). Virgin Tenax (or material to be recycled) is extracted in a Soxhlet apparatus for a minimum of 18 hours each time with acetone and hexane prior to preparation of cartridge samplers (2,5). After purification of the Tenax GC sorbent and drying in a vacuum oven at 100°C for 3 to 5 hours at 28 inches of water, all the sorbent material is meshed to provide a 35/60 particle size range. Cartridge samplers are then prepared and conditioned at 270°C with helium flow at 30 ml/min for 30 min. The conditioned cartridges are transferred to Kimax® (2.5 cm x 150 cm) culture tubes immediately sealed using Teflon-lined caps and cooled. This procedure is performed in order to avoid recontamination of the sorbent bed (2,5).

Cartridge samplers with longer beds of sorbent may be prepared using a proportional increased amount of Tenax in order to achieve a larger breakthrough volume for compounds of interest, and thus increasing the overall sensitivity of the technique (8).

6.2 Gas Chromatographic Column

A 0.35 mm i.d. x 100 m glass SCOT capillary column coated with SE-30 stationary phase and 0.1% benzyltriphenylphosphonium chloride is used for effecting the resolution of the volatile organic compounds (5). The capillary volume is conditioned for 48 hr at 245° at 2.25 ml/min of helium flow.

A glass jet separator on a Varian MAT CH-7 GC/MS/COMP system is employed to interface the glass capillary column to the mass spectrometer. The glass jet separator is maintained at 240°C (2,5).

6.3 Inlet Manifold

An inlet manifold for thermally recovering vapors trapped on Tenax sampling cartridges is used and is shown in Figure B.1 (1,2,4,5).

6.4 Gas Chromatograph

A Varian 1700 gas chromatograph is used to house the glass capillary column and is interfaced to the inlet manifold (Figure B.1).

6.5 Mass Spectrometry/Computer

A Varian MAT CH-7 mass spectrometer with a resolution of 2,000 equipped with a single ion monitoring capability is used in tandem with a gas chromatograph (Figure B.1). The mass spectrometer is interfaced to a Varian 620/L computer (Figure B.1).

7.0 Reagents and Materials

All reagents used are analytical reagent grade.

8.0 Procedure

8.1 Cleaning of Glassware

All glassware, sampling tubes, cartridge holders, etc. are washed in Isoclean/water, rinsed with deionized distilled water and acetone, and air dried. Glassware is heated to 450-500°C for 2 hr to insure that all organic material has been removed prior to its use.

8.2 Preparation of Tenax GC

Virgin Tenax GC is extracted in a Soxhlet apparatus for a minimum of 18 hr with acetone or methanol piror to its use. The Tenax GC sorbent is dried in a vacuum oven at 100°C for 3-5 hr and then sieved to provide a fraction corresponding to 35/60 mesh. This fraction is used for preparing sampling cartridges. In those cases where sampling cartridges of Tenax GC are recycled, the sorbent is extracted in a Soxhlet apparatus with acetone or methanol as described for the virgin material, but the sorbent is further extracted with a nonpolar solvent, hexane, in order to remove the relatively nonpolar and nonvolatile materials which might have accumulated on the sorbent bed during previous sampling periods.

B.3 Collection of Volatile Organics in Ambient Air

Continuous sampling of ambient air is accomplished using a Nutech Model 221-A portable sampler (Nutech Corp., Durham, NC, see Figure B.1 Reference 2). Flow rates between 1-10 l/min are available with this sampling system. Flow rates are generally maintained at 1 l using critical orifices, and the total flow is monitored through a calibrated flow meter. The total flow is also registered by a dry gas meter. Concomitant with these parameters the temperature is continuously recorded with a Meterological Research, Inc. Weather Station since the breakthrough volume is important in order to obtain quantitative data on the volatile organics. This portable sampling unit operates on a 12 volt storage battery and is capable of continuous operation up to a period of 24 hr. However, in most cases at the rates which are employed in the field, the sampling period is generally 1-3 hr. This portable sampling unit is generally utilized for obtaining "high volume" samples. Duplicate cartridges are deployed on each sampling unit utilizing a sampling head as shown in Figure B.2.

In addition to the Nutech samplers, DuPont personnel samplers are also used to acquire "low volumes" of ambient air as well as long-term integrated samples (12-36 hr). Identical Tenax FC sampling cartridges are employed in this case, and the sampling is conducted in duplicate. The flow rate is balanced between duplicate cartridges using critical orifices to maintain a rate of 25-100 ml/min per cartridge.

For large sample volumes, it is important to realize that a total volume of air may cause the elution of compounds through the sampling tube if their breakthrough volume is exceeded. The breakthrough volumes of some of the volatile organics are shown in Table B.2 (2,4,7,8). These breakthrough volumes have been determined by a previously described

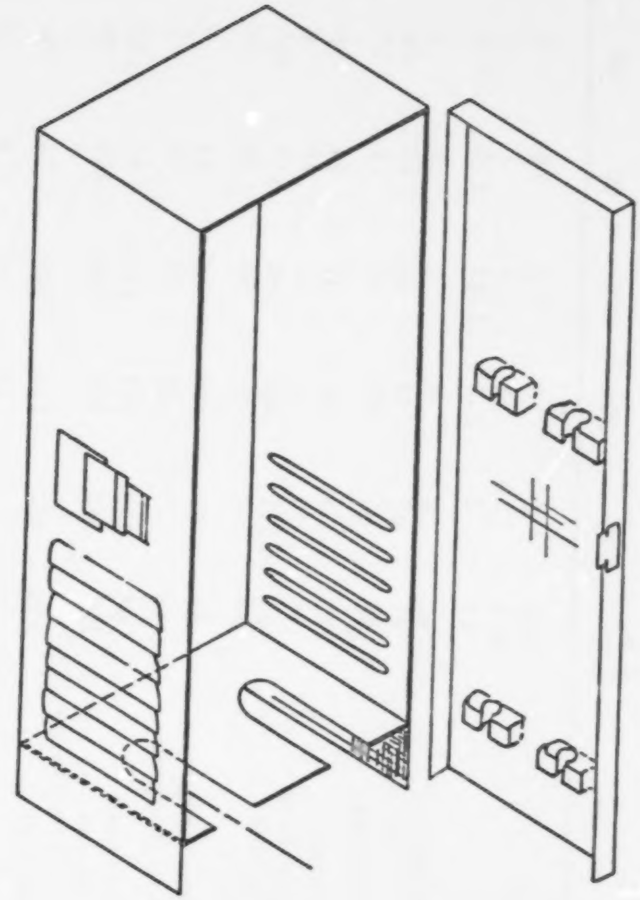


Figure B.2. Sampling head for housing cartridge sampling train.

Table B.2. TENAX GC BREAKTHROUGH VOLUMES FOR SEVERAL ATMOSPHERIC POLLUTANTS[1]

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
halogenated hydrocarbon	methyl chloride	-24	8	6	5	4	3	2.5
	methyl bromide	3.5	3	2	2	1	1	0.9
	vinyl chloride	13	2	1.5	1.25	1.0	0.8	0.6
	methylene chloride	41	11	9	7	5	4	3
	chloroform	61	42	31	24	18	13	10
	carbon tetrachloride	77	34	27	21	16	13	10
	1,2-dichloroethane	83	53	41	31	23	18	14
	1,1,1-trichloroethane	75	23	18	15	12	9	7
	tetrachloroethylene	121	361	267	196	144	106	78
	trichloroethylene	87	90	67	50	38	28	21
	1-chloro-2-methylpropene	68	26	20	16	12	9	7
	3-chloro-2-methylpropene	72	29	22	17	13	10	8
	1,2-dichloropropane	95	229	162	115	81	58	41
	1,3-dichloropropane	121	348	253	184	134	97	70
	epichlorohydrin (1-chloro-2,3-epoxypropane)	116	200	144	104	74	54	39
	3-chloro-1-butene	64	19	15	12	9	7	6
	allyl chloride	45	21	16	12	9	6	5
	4-chloro-1-butene	75	47	36	27	20	15	12
	1-chloro-2-butene	84	146	106	77	56	40	29
	chlorobenzene	132	899	653	473	344	249	181
	o-dichlorobenzene	181	1,531	1,153	867	656	494	372
	m-dichlorobenzene	173	2,393	1,758	1,291	948	697	510
	benzyl chloride	179	2,792	2,061	1,520	1,125	830	612
	bromoform	149	507	386	294	224	171	130
	ethylene dibromide	131	348	255	186	138	101	74
	bromobenzene	155	2,144	1,521	1,079	764	542	384

Table B.2. (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
halogenated ethers	2-chloroethyl ethyl ether	108	468	336	241	234	124	89
	Bis-(chloromethyl)ether	-	995	674	456	309	209	142
nitrosamines	N-nitrosodimethylamine	151	385	280	204	163	148	107
	N-nitrosodiethylamine	177	2,529	1,836	1,330	966	700	508
Oxygenated hydrocarbons	acrolein	53	19	14	10	8	6	4
	glycidaldehyde	-	364	247	168	114	77	52
	propylene oxide	34	35	24	17	11	8	5
	butadiene diepoxide	-	1,426	1,009	714	506	358	253
	cyclohexene oxide	132	2,339	1,644	1,153	811	570	400
	styrene oxide	194	5,370	3,926	2,870	2,094	1,531	1,119
	phenol	183	2,071	1,490	1,072	769	554	398
	acetophenone	202	3,191	2,382	1,778	1,327	991	740
	β-propiolactone	57	721	514	366	261	186	132
nitrogenous hydrocarbons	nitromethane	101	45	34	25	19	14	11
	aniline	184	3,864	2,831	2,075	1,520	1,114	817
sulfur compounds	diethyl sulfate	208	40	29	21	15	11	8
	ethyl methane sulfate	86	5,093	3,681	2,564	1,914	1,384	998
amines	dimethylamine	7.4	9	6	4	3	2	1
	isobutylamine	69	71	47	34	23	16	11
	_t_-butylamine	89	6	5	4	3	2	1
	di-(_n_-butyl)amine	159	9,506	7,096	4,775	3,105	2,168	1,462
	pyridine	115	378	267	189	134	95	67
	aniline	184	8,128	5,559	3,793	2,588	1,766	1,205
ethers	diethyl ether	34.6	29	21	15	11	8	5
	propylene oxide	35	13	9	7	5	4	3

Table B.2. (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
esters	ethyl acetate	77	162	108	72	48	32	22
	methyl acrylate	80	164	111	75	50	34	23
	methyl methacrylate	100	736	484	318	209	137	90
ketones	acetone	56	25	17	12	8	6	4
	methyl ethyl ketone	80-2	82	57	39	27	19	13
	methyl vinyl ketone	81	84	58	40	28	19	14
	acetophenone	202	5,346	3,855	2,767	2,000	1,439	1,037
aldehydes	acetaldehyde	20	3	2	2	1	0.9	0.7
	benzaldehyde	179	7,586	5,152	3,507	2,382	1,622	1,101
alcohols	methanol	64.7	1	1	0.8	0.6	0.4	0.3
	n-propanol	97.4	27	20	14	10	7	5
	allyl alcohol	97	32	23	16	11	8	6
aromatics	benzene	80.1	108	77	54	38	27	19
	toluene	110.6	494	348	245	173	122	86
	ethylbenzene	136.2	1,393	984	693	487	344	243
	cumene	152.4	3,076	2,163	1,525	1,067	750	527
hydrocarbons	*n*-hexane	68.7	32	23	17	12	9	6
	n-heptane	98.4	143	104	75	55	39	29
	1-hexene	63.5	28	20	15	11	8	6
	1-heptene	93.6	286	196	135	93	64	44
	2,2-dimethylbutane	49.7	0.5	0.4	0.3	0.2	0.2	0.1
	2,4-dimethylpentane	80.5	435	252	146	84	49	28
	4-methyl-1-pentene	53.8	14	10	8	6	4	3
	cyclohexane	80.7	49	36	26	19	14	10

Table B.2. (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F) 50	60	70	80	90	100
inorganic gases	nitric oxide	-	0	0	0	0	0	0
	nitrogen dioxide	-	0	0	0	0	0	0
	chlorine	-	0	0	0	0	0	0
	sulfur dioxide	-	0.06	0.05	0.03	0.02	0.02	0.01
	water	100	0.06	0.05	0.04	0.03	0.01	0

[1] Breakthrough volume is given in 1/2.2 g Tenax GC used in sampling cartridges.

technique (2). The breakthrough volume is defined as that point at which 50% of a discreet sample introduced into the cartridge is lost. Although the identity of a compound during ambient air sampling is not known (therefore, also its breakthrough volume), the compound can still be quantified after identification by GC/MS/COMP once the breakthrough volume has subsequently been established. Thus, the last portion of the sampling period is selected which represents the volume of air sampled prior to breakthrough for calculating their concentration. For cases when the identity of volatile organic compound is not known until after GLC/MS, the breakthrough volume is subsequently determined.

Previous experiments have shown that the organic vapors collected on Tenax GC sorbent are stable and can be quantitatively recovered from the cartridge samplers up to 4 weeks after sampling when they are tightly closed in cartridge holders and placed in a second container that can be sealed, protected from light, and stored at 0° C (1,2).

8.4 Analysis of Samples

The instrumental conditions for the analysis of volatile organics on the sorbent Tenax GC sampling cartridge are shown in Table 8.3. The thermal desorption chamber in the six-port valco valve is maintained at 270° and 240°, respectively. The glass jet separator is maintained at 240°. The mass spectrometer is set to scan the mass range from 25-350. The helium purge gas through the desorption chamber is adjusted to 15-20 ml/min. The nickel capillary trap on the inlet manifold is cooled with liquid nitrogen. In a typical thermal desorption cycle, a sampling cartridge is placed in the preheated desorption chamber and the helium gas is channeled through the cartridge to purge the vapors into the liquid nitrogen capillary trap [the inert activity of the trap has been shown in a previous study (5)]. After the desorption has been completed, the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 10°/min); the carrier gas then introduces the vapors onto the high resolution GLC column. The glass capillary column is temperature programmed from ambient to 240° C at 4° C/min and held at the upper limit for a minimum of 10 min. After all the

Table B.3. OPERATING PARAMETERS FOR GLC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	270°C
valve	220°C
capillary trap - minimum	-195°C
maximum	+180°C
thermal desorption time	4 min
GLC	
100 m glass SCOT-SE-30	25-240°C, 4/C° min
carrier (He) flow	∿3 ml/min
transfer line to ms	240°C
MS	
scan range	m/e 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	6.0
ion source vacuum	∿4 x 10^{-6} torr

components have been eluted from the capillary column, the analytical column is then cooled to ambient temperature and the next sample is processed (2).

An example of the analysis of volatile organics in ambient air is shown in Figure B.3 and the background from a blank cartridge is shown in Figure B.4. The high resolution glass capillary column was coated with SE-30 stationary which is capable of resolving a multitude of compounds to allow their subsequent identification by MS/COMP techniques; in this case over 120 compounds were identified in this chromatograph.

8.4.1 Operation of the MS/COMP System (Figure B.5)

Typically, the mass spectrometer is first set to operate in the repetitive scanning mode. In this mode the magnet is automatically scanned exponentially upward from a preset low mass to a high mass value. Although the scan range may be varied depending on the particular sample, typically the range is set from m/e 25 to m/e 300. The scan is completed in approximately 1.8 sec. At this time the instrument automatically resets itself to the low mass position in preparation for the next scan, and the information is accumulated by an on-line 620/L computer and written onto magnetic tapes or the dual disk system. The reset period requires approximately 2.0 sec. Thus, a continuous scan cycle of 3.8 sec/scan is maintained and repetitively executed throughout the chromatographic run. The result is the accumulation of a continuous series of mass spectra throughout the chromatographic run in sequential fashion.

Prior to running unknown samples, the system is calibrated by introducing a standard substance, perfluorokerosene, into the instrument and determining the time of appearance of the known standard peaks in relation to the scanning magnetic field. The calibration curve which is thus generated is stored in the 620/L computer memory. This calibration serves only to calibrate the mass ion over the mass scanning range.

While the magnet is continuously scanning, the sample is injected and automatic data acquisition is initiated. As each spectrum is acquired by the computer, each peak which exceeds a preset threshold is recognized and reduced to centroid time and peak intensity. This information is

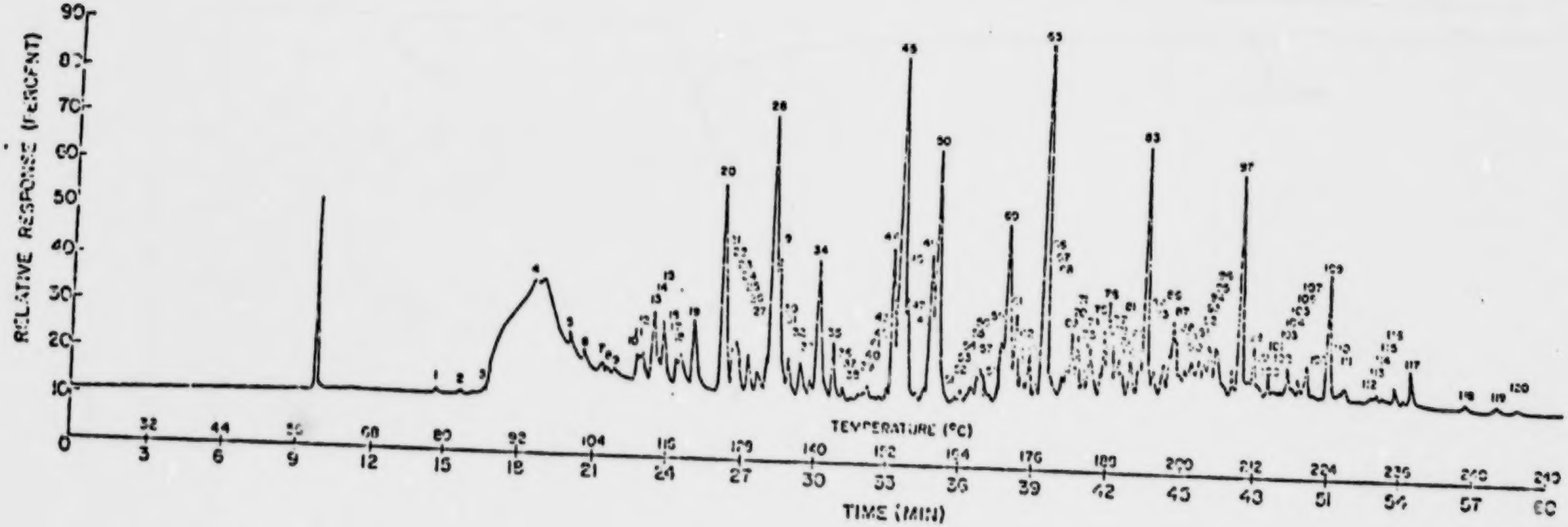


Figure B.3. Profile of ambient air pollutants for Wood River, IL using high resolution gas chromatography/mass spectrometry/computer.

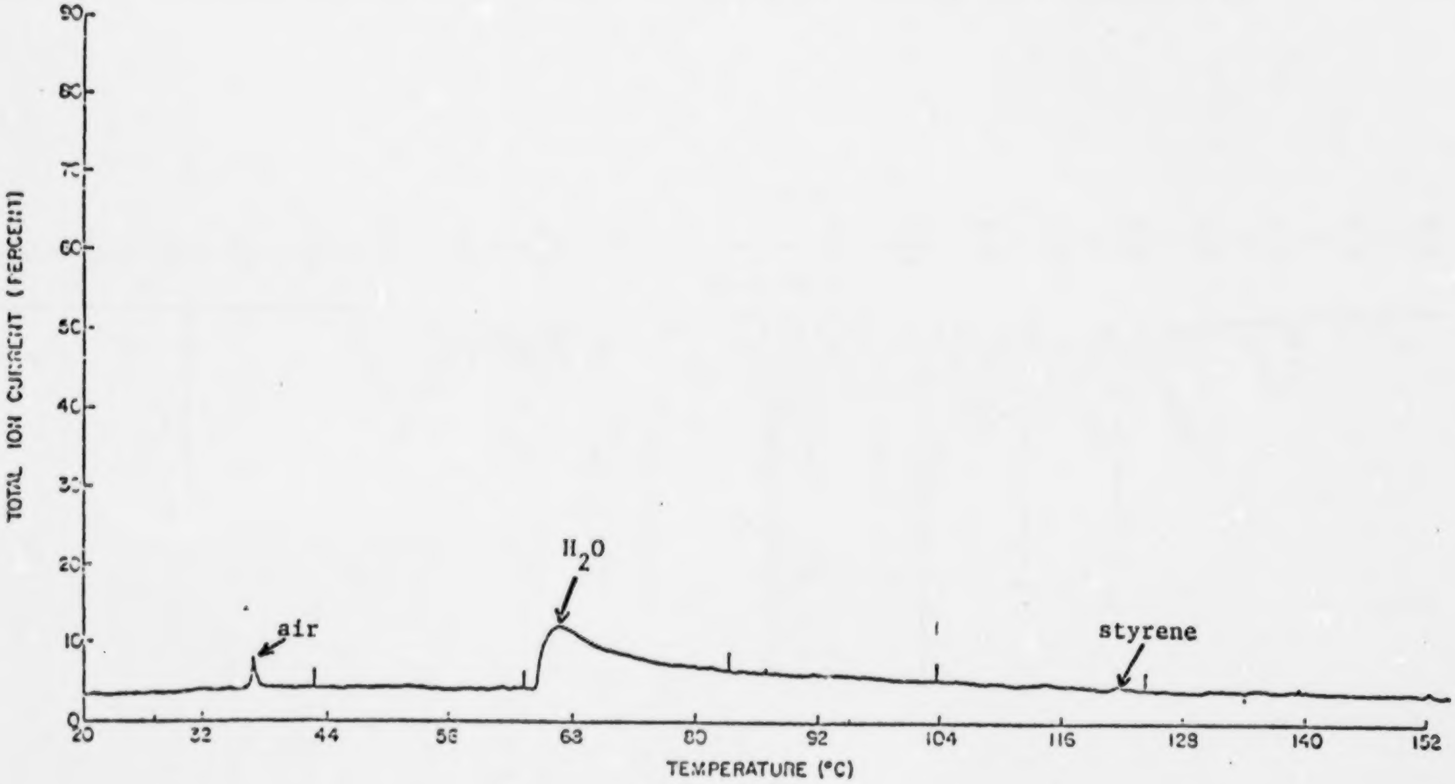


Figure B.4. Background profile for Tenax GC cartridge blank

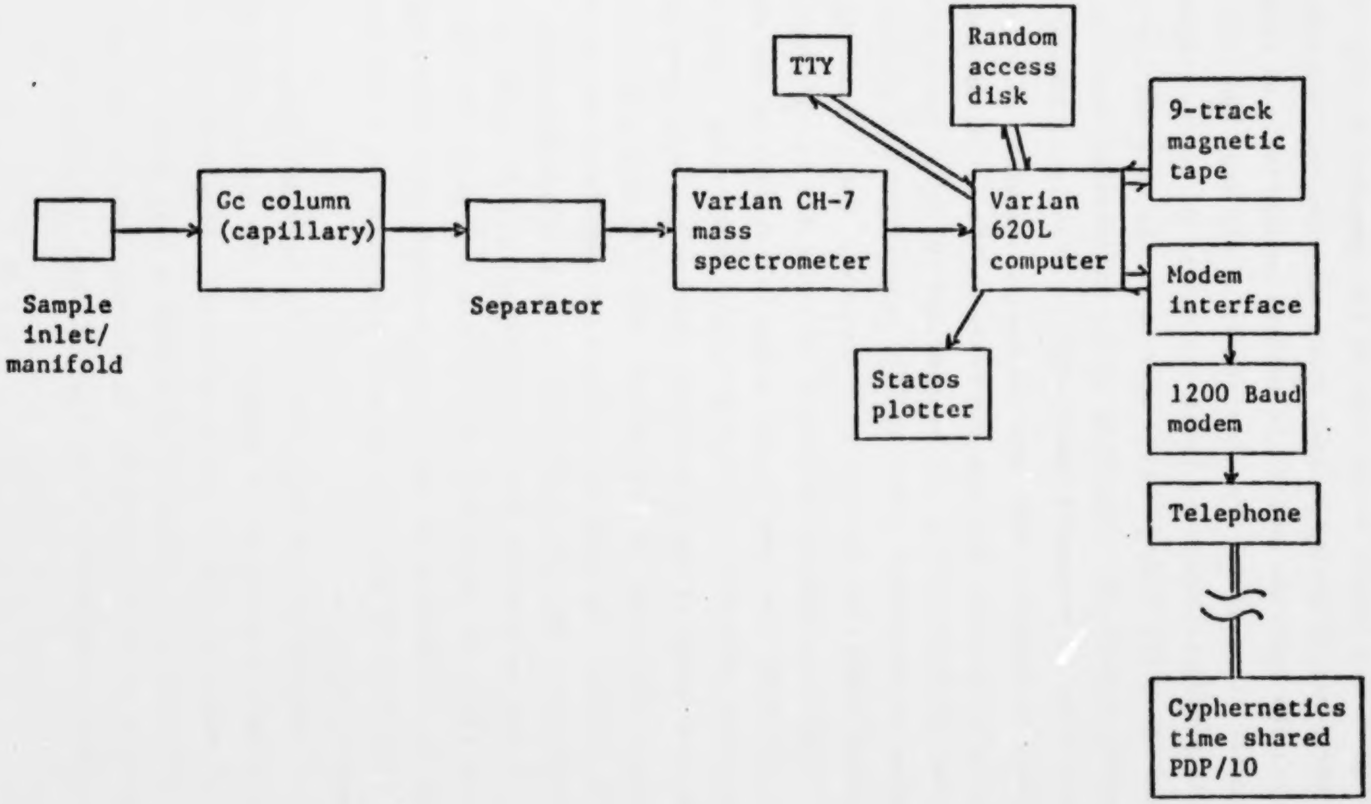

TTY
Random access disk
9-track magnetic tape
Gc column (capillary)
Varian CH-7 mass spectrometer
Varian 620L computer
Modem interface
Sample inlet/ manifold
Separator
Statos plotter
1200 Baud modem
Telephone
Cyphernetics time shared PDP/10

Figure B.5. Schematic diagram of GC-MS computer system.

stored in the computer core while the scan is in progress. In addition, approximately 30 total ion current values and an equal number of Hall probe signals are stored in the core of the computer as they are acquired. During the 2-second period between scans this spectral information, along with the spectrum number, is written sequentially on disks, and the computer is reset for the acquisition of the next spectrum.

This procedure continues until the entire GC run is completed. By this time there are from 800-1400 spectra on the disk which are then subsequently processed. Depending on the information required, that day may then either be processed immediately or additional samples may be run, stored on magnetic tape, and the results examined at a later time.

The mass spectral data are processed in the following manner. First, the original spectra are scanned and the total ion current (TIC) information is extracted. Then the TIC intensities are plotted against the spectrum number on the Statos 31 recorder. The information will generally indicate whether the run is suitable for further processing, since it provides some idea of the number of unknowns in the sample and the resolution obtained using the particular GLC column conditions.

The next stage of the processing involves the mass conversion of the spectral peak times to peak masses, which is done directly via the dual disk system. The mass conversion is accomplished by use of the calibration table obtained previously using perfluorokerosene. Normally one set of the calibration data is sufficient for an entire day's data processing since the characteristics of the Hall probe are such that the variation in calibration is less than 0.2 atomic mass units/day. A typical time required for this conversion process for 1,000 spectra is approximately 30 min.

After the spectra are obtained in mass converted form, processing proceeds either manually or by computer. In the manual mode, the full spectra of scans for the GC run are recorded on the Statos 31 plotter. The TIC information available at this time is most useful for deciding which spectra are to be analyzed. At the beginning of the runs where peaks are very sharp nearly every spectrum must be inspected individually to determine the identity of the component. Later in the chromatographic run when the peaks are broader only selected scans need to be analyzed.

Identification of resolved components is achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra. (9). Individual difficult and unknowns are searched by the use of the Cornell University STIRS and PBM systems. Unknowns are also submitted to EPA MSSS system for identification. When feasible, the identification of unknowns are confirmed by comparing the cracking pattern and elution temperatures for two different chromatographic columns (SE-30 and Carbowax SCOT capillaries) for the unknown and authentic compounds. The relationship between the boiling point of the identified halogenated hydrocarbon and the elution temperature on a nonpolar column (the order of elution of constituents is predictable in homologous series since the SE-30 SCOT capillary separates primarily on the basis of boiling point) is carefully considered in making structure assignments.

Mass spectral search programs are operational at the Triangle Universities Computation Center (TUCC). RTI maintains twice daily service to TUCC, which is one-quarter mile distance from the RTI campus. Additional information about each magnetic tape containing the mass spectra of halogenated hydrocarbons is entered directly into the TUCC job stream using a remote job entry processing. This is normally done at TUCC using one of the five terminals located within the Analytical Sciences Laboratory. The control information contains selected spectrum numbers of instructions to process entire gc runs. The computer program systems compare simultaneously either the entire library of 25,000 compounds or some subset of this library. The complete reports showing the best fits for each of the unknowns is produced at TUCC and printed out at the high speed terminals located on the RTI campus of TUCC. Thus, the processing of the mass spectral data obtained for the halogenated hydrocarbons in the samples collected is processed by one of three routes. Each consists of a different level of effort. The first level is strictly a manual interpretation process which proves to be the most thorough approach. The second level is executed when the interpretation at the first level has not yielded conclusive results.

8.4.2 Quantitative Analysis

In many cases the estimation of the level of pollutants by capillary gas chromatography in combination with mass spectrometry is not feasible utilizing only the total ion current monitor (See Figure B.3 for example). Since baseline resolution between peaks is not always achieved, we employ the techniques which have been previously developed under contract whereby full spectra are obtained during the chromatographic separation step and the selected ions are presented as mass fragmentograms using computer software programs which allow the possibility of deconvoluting constituents which were not resolved in the total ion current chromatogram (6). Examples are depicted in Figures B.6 and B.7 which represent an ambient air sample with a TIC profile as in Figure B.3.

In our GC/MS/COMP system, we request from the Varian 620/L dedicated computer mass fragmentograms for any combination of m/e ions when full mass spectra are obtained during chromatography. Thus, selectivity is obtained by selecting the unique ion for that particular organic substance, and this is represented vs. time with subsequent use of that ion intensity for quantitation. Also, quantification with external standards is easily achieved using the intensity of the total ion current monitor or the use of a unique mass cracking ion in a mass spectrum of the external standard. Thus, we use mass fragmentography for the quantitation of organics in ambient air when the total ion current monitor is inadequate because of the lack of complete resolution between components in the mixture.

As described previously, the quantitation of constituents in ambient air samples is accomplished either by utilizing the total ion current monitor or, where necessary, the use of mass fragmentograms. In order to eliminate the need to obtain complete calibration curves for each compound for which quantitative information is desired, we use the method of relative molar response (RMR) factors (10). Successful use of this method requires information on the exact amount of standard added and the relationship of RMR (unknown) to the RMR (standards). The method of calculations is as follows:

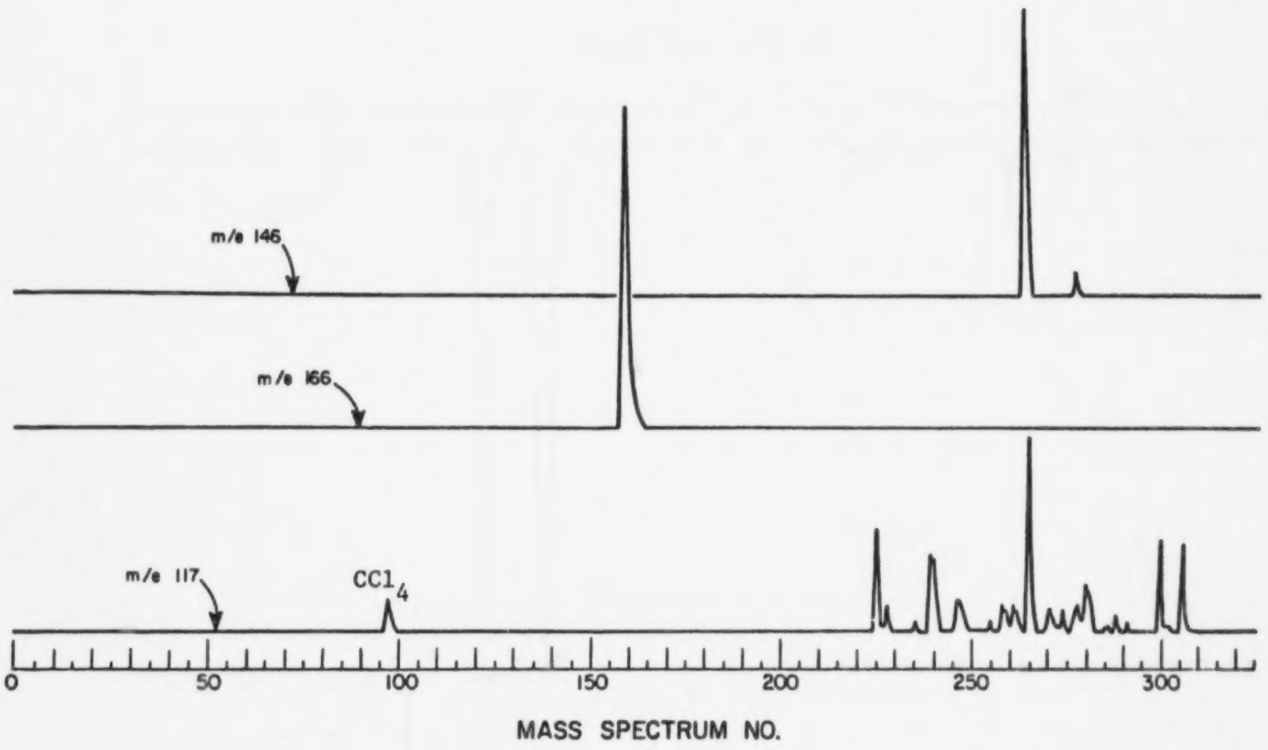


Figure B.6. Mass fragmentograms of characteristic ions representing carbon tetrachloride (m/e 117), tetrachloroethylene (m/e 166) and m-dichlorobenzene (m/e 146) in ambient air.

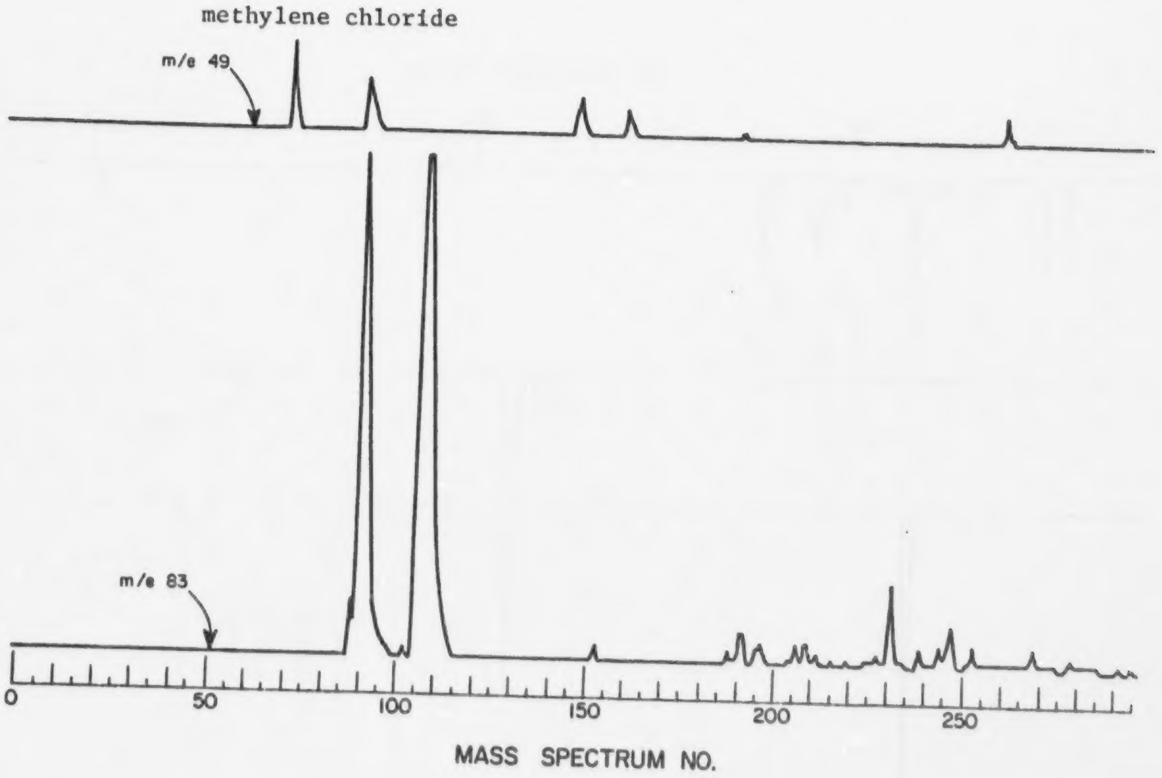


Figure B.7. Mass fragmentograms of characteristic ion representing methylene chloride (m/e 49) and chloroform (m/e 83) in ambient air.

$$(1)\quad RMR_{unknown/standard} = \frac{A_{unk}/Moles_{unk}}{A_{std}/Moles_{std}}$$

A = peak area, determined by integration or triangulation.

The value of RMR is determined from at least three independent analyses.

$$(2)\quad RMR_{unk/std} = \frac{A_{unk}/g_{unk}/GMW_{unk}}{A_{std}/g_{std}/GMW_{std}}$$

A = peak area, as above
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$(3)\quad g_{unk} = \frac{A_{unk} \cdot GMW_{unk} \cdot g_{std}}{A_{std} \cdot GMW_{std} \cdot RMR_{unk/std}}$$

The standard added can be added as an internal standard during sampling, however, since the volume of air taken to produce a given sample is accurately known, it is also possible and more practical to use an external standard whereby the standard is introduced into the cartridge prior to its analysis. Two standards, hexafluorobenzene and perfluorotoluene, are used for the purpose of calculating RMR's. From previous research it has been determined that the retention times for these two compounds are such that they elute from the glass capillary column (SE-30) at a temperature and retention time which does not interfere with the analysis of unknown compounds in ambient air samples.

Since the volume of air taken to produce a given sample is accurately known and an external standard is added to the sample, then the weight can be determined per cartridge and hence the concentration of the unknown. The approach for quantitating ambient air pollutants requires that the RMR is determined for each constituent of interest. This means that when an ambient air sample is taken, the external standard is added during the analysis at a known concentration. It is not imperative at this point to know what the RMR of each of the constituents in the sample happens to be, however, after the unknowns are identified. Then the RMR can be subsequently determined and the unknown concentration calculated in the original sample using the RMR. In this manner it is possible to obtain qualitative and quantitative information on the same sample with a minimum of effort.

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Analytical protocol revised 1/24/77.

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